THE UNIVERSITY *of* EDINBURGH

The Crystal Structure of some Sugar Compounds.

d-Mannitol and d-Mannose.

by

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C O N T E N T S.

I N T R O D U C T I O N.

The results of X-ray analysis of crystals have led, in a large number of cases, to a complete solution of the molecular structure of the compounds in question, and it was thought that an investigation of the crystal structure of some of the sugars would lead to an elucidation of the structure of the sugar molecule.

It has been shown by ordinary chemical means, that the molecule of d-Mannitol has a comparatively simple structure. Moreover, it is a compound which is readily obtained in the form of good crystals. For this reason an investigation of the crystal structure of d-Mannitol was undertaken, the results obtained from that compound being compared with those obtained from the corresponding sugar - d-Mannose.

The methods of X-ray analysis are fully discussed in Bragg's "X-rays and Crystal Structure", and in Wyckoff's "The Structure of Crystals", but a brief account of the methods used will be given.

According to the type of work to be carried out, use is made of one or more of the four chief methods of X-ray analysis.

(a) The Bragg Ionisation Spectrometer Method;

(b) The Debye and Scherrer Powder Method;

(c) The Laue Method;

(d) The Single Crystal Rotation Method of Rinne, Schiebold and Polyani.

(a). The ionisation spectrometer was originally designed to measure, one at a time, the reflections of X-ray beams by the different sets of planes within the crystal. A narrow pencil of X-rays (AB) falls on a crystal face, (C), the crystal being mounted on a rotating table, the orientation of which is observed on a scale and vernier. When a reflection occurs, the reflected beam is received in an ionisation chamber, (D), filled with a gas which ionises readily under the action of the particular kind of X-rays in use. The ionisation chamber rotates about the same axis as the crystal table, and the orientation of the chamber from the undeflected beam of X-rays is the measure of twice the glancing angle θ. The calculation of the spacing d of the plane from which the measurements are made, is then a simple application of the Bragg law,

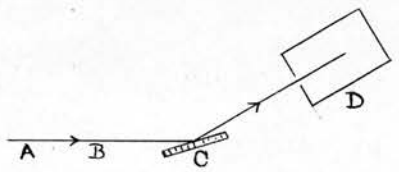


Fig. 1.

$$n\lambda = 2d.\sin\theta$$

where n is the order of the spectrum measured, and λ is the wavelength of the monochromatic X-rays used. The ionisation current gives a measure of the intensity of the reflected beam of X-rays.

One of the important properties of the ionisation spectrometer is that it measures not only the spacings of sets of planes, but also the angle between any two

sets of planes.

(b). The Debye and Scherrer method is an adaptation of the Bragg ionisation spectrometer method. The single crystal is replaced by a glass plate on whose surface is a layer of powdered crystals, and the ionisation chamber is replaced by a photographic plate or film. The layer of powdered crystals is oscillated through a small angle, and a narrow beam of monochromatic X-rays is directed on to the layer at the axis of oscillation, the reflected beams being recorded on the photographic plate.

In the layer of powdered substance there are minute crystals orientated in all possible directions about the axis, and with respect to the incident rays, so that the photographs must be alike in all aspects round the centre. The distance of the plate or film from the axis of oscillation is known, and, if the position of any line on the photograph is measured, it is then possible to calculate the spacing of the plane corresponding to the reflection by means of the Bragg law.

(c). The method devised by Laue was the first to be used in X-ray analysis.

A fine pencil of heterogeneous X-rays is passed through a thin crystal plate in a direction which is perpendicular to a known set of crystallographic planes, and the reflections recorded on a flat photographic plate which is also perpendicular to the direction of the incident beam of X-rays.

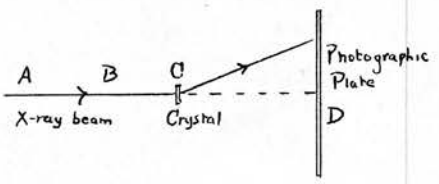


Fig. 2.

As the crystal is at rest during the exposure of the plate, the angle between the incident beam and each set of planes is a fixed quantity. The flexibility required in the relative values of $\underline{d}$, $\underline{\lambda}$, and $\underline{\theta}$, if the equation $n\lambda=2d.\sin\theta$ is to be satisfied, is supplied by the variability of the wavelength of the X-rays.

(d). The method of the rotating crystal, devised by Rinne, Schiebold, and Polyani, is especially useful in the analysis of the structure of a crystal.

A crystal is mounted on a fine glass fibre and slowly rotated about a vertical axis. A horizontal beam of monochromatic X-rays impinges on the crystal. The diffracted beams fall on a flat photographic plate or on a film bent into the form of a cylinder whose axis coincides with the axis of rotation of the crystal.

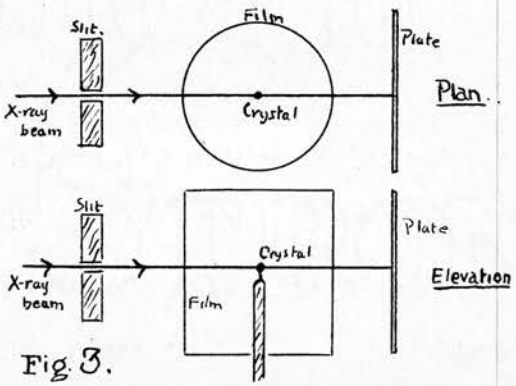


Fig. 3.

On rotation of the crystal, one set of planes after another is brought to such an angle $\underline{\theta}$ with the incident beam, that the law of reflection is satisfied, and reflection takes place. A photograph shows a collection of spots lying on ordered lines (Schiebold's "Schichtlinien" or Layer Lines).

When a plane comes into the reflecting position it will reflect four times in a complete revolution of the crystal. Thus in the rotation photograph, spots appearing on the right hand half will also appear on the left hand half . Such a photograph will be symmetrical about a horizontal line. The four spots corresponding

to any set of planes lie, therefore, at the corners of a rectangle, in which, if the distance from the centre of the rectangle to the corner is r, and the distance of the plate from the crystal rotation axis is D, the glancing angle θ is given by

$$\tan 2\theta = r/D$$

in the case of a flat plate, and hence the spacing d of a particular set of planes can be calculated from the Bragg law, as before.

Further, if the crystal be rotated about a known crystallographic axis, the first layer line corresponds to the first order reflection from that set of planes for which the index corresponding to the axis of rotation is unity. Thus by making photographs about each of the crystallographic axes in turn, the dimensions of the unit cell may be determined unequivocally.

It is for this reason that the rotating crystal method is the most useful in an X-ray analysis.

The ionisation spectrometer method gives very much more accurate results, but it is much more laborious to use, on account of the fact that it is possible to deal with only one set of planes at a time. In most crystals the reflections from several hundred sets of planes may be found, and in such a case the advantages of greater accuracy are outweighed.

The powder method involves a knowledge of the dimensions of the unit cell for its use, and the method is of little use in a preliminary investigation. The measurement of the intensity of a reflected ray from powder photographs is very unsatisfactory, since it may

happen that a larger number of micro-crystals are orientated in one direction than in another. This, of course, leads to an increased intensity, where such may not be explained by the arrangement of the atoms within the crystal. The thickness of the layer of crystals also affects the intensity of the reflected beams, since the incident beam does not always impinge on the mass of crystals at the axis of oscillation, and hence some of the reflected beam may be absorbed by the crystals through which it has to pass. This lack of coincidence of the incident beam and the axis of oscillation causes an alteration of the distance of the crystals from the photographic plate, and a corresponding displacement of the line produced by the reflected beam on the plate occurs. An error in the calculation of the spacing is thus introduced.

Since the wavelength of the X-rays causing a spot on a Laue photograph is not known, calculation of the spacing of the set of reflecting planes is impossible unless the dimensions of the unit cell are known. Thus the method is of little use in a preliminary investigation, but considerable information may be obtained of the symmetry of the crystal structure. An adaptation of the method is used in the setting of a crystal in a definite orientation on the spectrometer.

In an analysis of crystal structures by any of the methods at present in use, the experimental data are all comprised in a knowledge of the intensities of X-ray reflections from every one of a series of

of planes in a crystal. The procedure in an analysis can be conveniently divided into three stages.

1. The determination of the size and shape of the unit cell of the fundamental lattice of the crystal.
2. The determination of the indices of the reflecting planes, leading to a determination of the space group.
3. The measurement of the intensity of reflection from each plane, leading to a complete determination of the structure.

The rotating crystal method is best suited to the first two stages, and is now being extended to the third. A description of the derivation of the method will now be given.

Suppose the crystal is rotated about a principal crystallographic axis AB=a, the primitive translation. Suppose ED, GF, are traces of two consecutive planes, the h index of which is unity.

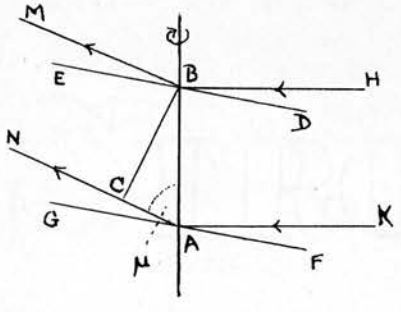


Fig. 4.

The axis of rotation is XABY and the beam of X-rays HB, KA, is perpendicular to this axis, and is reflected along BM, AN, (not necessarily in the plane of the paper, since DE and GF are traces of crystal planes). BC is perpendicular to AN, and the angle NAB is the angle μ.

Then, according to the laws of interference

phenomena, for a maximum at the first order reflection, the path difference AC, between the rays along KAN and along HBM, must be equal to the wavelength λ of the monochromatic X-rays in use. $AC = \lambda$. Hence it follows that

$$\cos\mu = AC/AB = \lambda/a$$

or $$a.\cos\mu = \lambda$$

Now in any given crystal a is constant, and λ is constant, hence μ is constant for all planes of the crystal lattice for which the h index is unity. Therefore all planes of the form (1,k,l) give reflections which lie on a cone about the axis of rotation, the angle of the cone being μ. For planes of the form (2,k,l) the relation is

$$a.\cos\mu_2 = 2\lambda$$

since a plane passes through A and B, and the mid-point of AB.

In general, for the nth. cone of reflection we have

$$a = \frac{n\lambda}{\cos\mu_n} \quad . \quad . \quad . \quad (I).$$

Whence, if n, λ, and μ are known, the primitive translation a can be evaluated.

These cones of reflection intersect a flat photographic plate set at right angles to the incident beam of X-rays in hyperbolae; on a cylindrical film the traces of the cones of reflection appear as straight lines. The lines in both cases are the Layer Lines. If the distance of the vertex of the nth, hyperbola from the central line of a flat plate is y, and the distance of the plate from the axis of rotation of the

crystal is D, then we have

$$\tan\mu = D/y \quad . \quad . \quad . \quad (II).$$

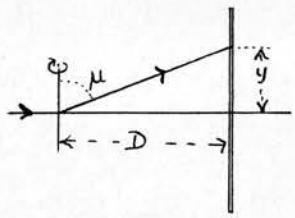


Fig. 5.

In the case of a cylindrical film, the distance of the nth. layer line from the zero layer line is y, and the radius of the cylinder into which the film is bent, is D, then we have as before

$$\tan\mu = D/y.$$

Thus μ can be determined from the photographs by measurement, and hence the value of a may be deduced from equation (I), using the appropriate values of n and y.

Planes of a given spacing d, give reflected rays which lie on a cone about the incident beam, the angle of the cone being 2θ, where $n\lambda = 2d.\sin\theta$. Consequently spots corresponding to planes of a given spacing lie on circles about the central spot, the radius being given by $r = D.\tan 2\theta$, in the case of a flat plate. Thus, if on the three photographs taken with rotation about the three crystallographic axes, one can find spots of equal intensity, and at the same distance from the central spot in each case, one can usually assume that the same set of planes is responsible for each spot in question, and the indices of that plane can be immediately obtained from the hyperbolae on which the spots lie.

In many cases it is necessary to obtain the spots corresponding to planes of high indices, and for this purpose a cylindrical camera is used. The curves of equal spacing are then ovals.

Having obtained the dimensions of the unit cell from measurements made on photographs made with rotation about each of the three crystallographic axes, the next step is to identify the planes which give rise to the spots. This may be done by the method which is now described.

Suppose the co-ordinates of a spot are L and y (Diagram is a projection of the solid figure on to the plane of the paper, and y is measured perpendicular to the paper).

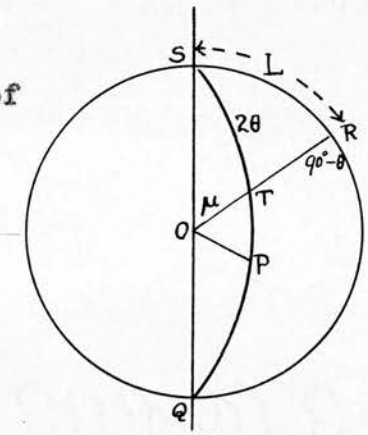


Fig. 6.

The axis of rotation is perpendicular to the paper through O. QO is the direction of the incident beam of X-rays, OR is the projection of the reflected beam and P is the pole of the reflecting plane, so that SPQ is the projection of the great circle containing the incident and reflected beams. Then, clearly,

$$OT = \mu$$

$$ST = 2\theta$$

$$SR = L$$

and from the triangle STR, we have that

$$\cos 2\theta = \cos L . \sin \mu \quad \ldots\ldots \text{(III)}.$$

If the radius of the camera is D, then equation (II) is true, and hence μ, and $\cos\mu = \lambda/a$ are known.

In the case of the Rhombic System of crystals, it can be shown by Co-ordinate Geometry, that the spacing of any plane (h,k,l), is given by

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad \ldots\ldots \text{(IV)}.$$

or $$d = \frac{abc}{(h^2.b^2.c^2 + k^2.a^2.c^2 + l^2.a^2.b^2)^{\frac{1}{2}}} \quad \ldots (V).$$

where a, b, c, are the primitive translations, and d is the spacing of the plane whose indices are h, k, and l.

Now $d = n\lambda/2\sin\theta$, and substituting this value of d in equation (IV), we obtain

$$2\sin^2\theta = \frac{h^2\lambda^2}{2a^2} + \frac{k^2\lambda^2}{2b^2} + \frac{l^2\lambda^2}{2c^2}$$

assuming that n is unity, i.e. we are dealing with the first order reflection.

Then from equation (III), we have

$$\cos L.\sin\mu = 1 - \left\{\frac{h^2\lambda^2}{2a^2} + \frac{k^2\lambda^2}{2b^2} + \frac{l^2\lambda^2}{2c^2}\right\}$$

or in general

$$\cos L = A - h^2.B - k^2.C - l^2.D \quad \ldots (VI).$$

where

$$A = \operatorname{cosec}\mu$$

$$B = \lambda^2/2a^2 .\sin\mu$$

$$C = \lambda^2/2b^2 .\sin\mu$$

$$D = \lambda^2/2c^2 .\sin\mu$$

When the unit cell has been determined, the values of A, B, C, and D may be calculated, and a diagram may be constructed on an appropriate scale showing the position of the spots for each layer line. Then, by superposition of the photograph on the diagram, the indices of the spots may be read off. The scheme is indicated in figure 7 where the first line contains the spots from the planes (1,0,0), (1,0,1), (1,0,2), etc.

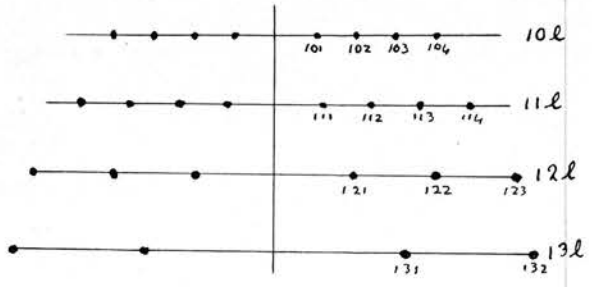


Fig. 7.

The second line contains the spots from the planes (1,1,0), (1,1,1), (1,1,2), etc., and so on for all the layer lines.

It will generally be found that certain values of h, k, l, give values of cosL which do not lie between +1 and -1. These planes do not come into the reflecting position

In some cases ambiguities occur when two or more spots lie very close together. In order to distinguish between the planes giving rise to these spots, use is made of a method in which the single crystal is oscillated through a small angle. Fuller reference will be made to this method later.

It is also possible to calculate the theoretical spacings of all planes which come into the reflecting position in another way.

The number of molecules in the unit cell may be found from the equation

$$abc\rho = N.M.1{\cdot}65 \quad \ldots\ldots \text{(VII)}.$$

where a, b, c, are the primitive translations, ρ is the density of the crystal, M is the molecular weight of the substance, 1·65 is a constant, and N is the number of molecules in the unit cell.

Combining equations (V) and (VII) we obtain

$$d = \frac{NM.1{\cdot}65}{\rho(h^2.b^2.c^2+k^2.a^2.c^2+l^2.a^2.b^2)^{\frac{1}{2}}} \quad \ldots \text{(VIII)}$$

Assuming a definite number of molecules N in the cell, it will generally be found that many of the calculated spacings agree with the measured values, while others may be twice or half as large as the measured spacings.

When such doublings or halvings occur, it is obvious that the dimensions of the unit cell used are not correct, and observation of the regularity of the doublings or halvings will show which of the axes is not of the correct dimensions.

The number of planes in a crystal, which come into the reflecting position during a complete rotation about a crystallographic axis, is limited. The method used to determine the possible reflecting planes involves the use of the reciprocal lattice diagram. The idea of a reciprocal lattice was first applied to the interpretation of the phenomena of crystal diffraction of X-rays by Ewald. (Z. f. Kryst. vol.56, p 129, 1921)

If the crystal is considered to be a simple space lattice, we may choose one point of the lattice as origin, and take the three vectors a, b, and c, as three primitive translations. It is possible to represent any plane of this lattice by the indices h, k, l, where the intercepts of such a plane on the primitive translations a, b, c, are a/h, b/k, c/l, respectively. Only those planes for which h, k, l, are integers (not necessarily prime to each other) are referred to here: i.e. in any set of parallel crystallographic planes the one nearest the origin is chosen, since it gives rise to the first order X-ray reflections. Those planes which are parallel to this, but whose distances from the origin are sub-multiples of its distance from the origin, give rise to reflections of a higher order.

From the planes of the lattice, defined as above, another lattice may be built up. Each point of this

lattice lies on the normal from the origin to a plane and at a distance ρ from the origin, where ρ and the spacing d of the set of planes are related by

$$\rho.d = k^2 \quad \ldots\ldots\ldots \text{(IX)}.$$

where k is a constant. Each point of the new lattice is thus the reciprocal polar of a plane in the old lattice in a sphere of radius k. Hence the new lattice is the reciprocal lattice of the old, and for every plane in the one there corresponds a point in the other, and vice versa.

The reciprocal lattice may be referred to a set of vectors, a^*, b^*, c^*, reciprocal to the set a, b, c, where, in general,

$a^* = \frac{k^2.bc}{\Delta} \sin\alpha$ and is perpendicular to the plane bc,

$b^* = \frac{k^2.ca}{\Delta} \sin\beta$ and is perpendicular to the plane ca,

$c^* = \frac{k^2.ab}{\Delta} \sin\gamma$ and is perpendicular to the plane ab,

where Δ is the volume of the parallelepipedon abc.

If we then build up a lattice with a^*, b^*, c^*, as the primitive translations, it will be the reciprocal lattice of that built up on a, b, and c. Then, if (h,k,l) are the indices of any plane in the original lattice, the corresponding point in the reciprocal lattice has h, k, l, for co-ordinates.

It is difficult to obtain a physical picture of the phenomena in the reciprocal lattice corresponding to the diffraction of X-rays in a crystal, but it is possible to obtain a geometrical one, if we assume Bragg's law.

Reflection takes place in the original lattice only if $\sin\theta = \lambda/2d$, where θ is the angle between the reflecting plane and the normal to the wave-front of the incident beam of X-rays. In the reciprocal lattice the wave-fronts become points travelling along their normal, and θ becomes the angle between the incident ray and the plane through the corresponding point in the reciprocal lattice, which is perpendicular to its radius vector. It has already been shown that the radius vector ρ is equal to k^2/d, so that the analogue of Bragg's law becomes

$$\sin\theta = \lambda\rho/2k^2 \quad \ldots\ldots\ldots \quad (X).$$

The geometrical conception of the reflection of X-rays is shown in figure 8, where, if a sphere of radius $2k^2/\lambda$ cuts the plane PQR, drawn through the point P normal to its radius vector PO, in the circle QR, then the angle OQP satisfies the law $\sin.OQP = \lambda\rho/2k^2$,

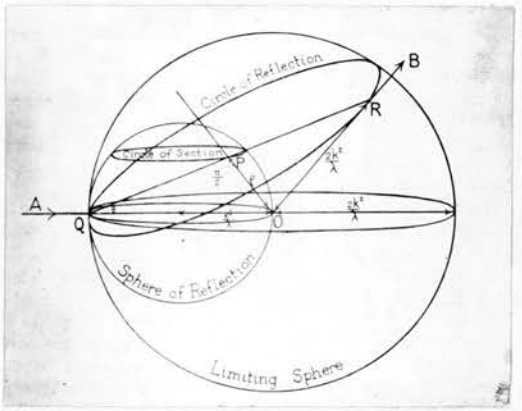


Fig. 8.

and hence the direction of a ray reflected by a plane in the original lattice corresponding to the point P lies along AO, and the reflected ray along OB. All rays which P can reflect lie along the cone OQR, of which the incident and reflected rays are diametrically opposite generators. Bernal, in "X-ray, Single Crystal, Rotation Photographs" (Proc. Roy. Soc., A, Vol. 113, 1926) states the law of reflection of X-rays by a point in the reciprocal

lattice thus:-

"A ray is reflected by a given point of the reciprocal lattice if, and only if it lies along a generator of a cone (the Cone of Reflection), whose apex is the origin, and whose base is the circle (the Circle of Reflection), which is the intersection of the plane through the point normal to its radius vector, and a sphere (the Limiting Sphere), whose centre is the origin, and whose radius is $2k^2/\lambda$."

It can be seen from the figure, that no point outside the limiting sphere can form a cone of reflection, and hence the plane of the original lattice corresponding to the point cannot reflect. The number of reflecting points (and hence planes), thus varies with the volume of the limiting sphere;,i.e. varies inversely as λ^3.

In the foregoing discussion the possible directions of the incident rays reflected from a point P of the reciprocal lattice were considered. It is possible to consider the possible positions of the points of the reciprocal lattice, which reflect for a given position or direction of the incident ray. It is obvious from the figure, that all points on the sphere QPO satisfy the condition $\sin\theta = \lambda\rho/2k^2$, and therefore this sphere is the locus of all points reflecting for the direction AO of the incident ray. This may be stated in another way:-

A point in the reciprocal lattice reflects a given ray only if it lies on the surface of the sphere of reflection, which has for diameter the ray which passes

through the origin, and whose radius is k^2/λ .

The occurrence of a reflection may be regarded as the intersection of the sphere of reflection and a point of the reciprocal lattice. These intersections form a three dimensional scheme, which may be projected on to the equatorial plane. This projection is made use of in determining the planes within the crystal which can reflect the incident X-rays.

In the use of the reciprocal lattice with homogeneous X-rays, it is convenient to choose for $\underline{k}$ the value $\underline{\lambda}$, the wavelength of the X-rays. The radius of the limiting sphere then becomes 2, and that of the sphere of reflection 1.

The use of the reciprocal lattice diagram in determining the possible reflecting planes is described in the case of an orthorhombic crystal which is rotated about its $\underline{b}$ axis. On a diagram with two mutually perpendicular axes $\underline{X}$ and $\underline{Y}$, (figure 9), cut off portions along the $\underline{X}$ axis equal to $\underline{a}^*$, $2\underline{a}^*$, $3\underline{a}^*$,..... $\underline{na}^*$, using some suitable scale.

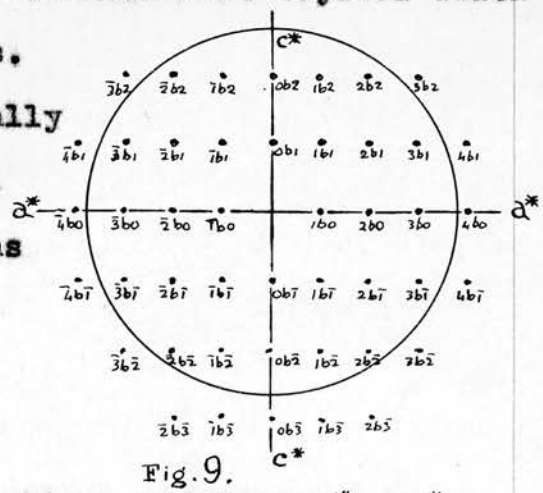


Fig.9.

Along the $\underline{Y}$ axis cut off portions equal to $\underline{c}^*$, $2\underline{c}^*$, $3\underline{c}^*$,.....$\underline{nc}^*$, on the same scale, where $a^* = \lambda/a$, $c^* = \lambda/c$, If lines are drawn parallel to the axes $\underline{X}$ and $\underline{Y}$, respectively, through the points $\underline{a}^*$, $2\underline{a}^*$, $\underline{c}^*$, $2\underline{c}^*$, etc. the intersections of these lines represent the points

of the reciprocal lattice, which in turn represent the planes within the crystal. Then with the origin as centre, and radius equal to unity on the same scale describe a circle. Then only the points of the projection of the reciprocal lattice which lie within this circle correspond to the crystal planes capable of reflecting the incident beam of X-rays.

In the case of the orthorhombic type of crystal where the b axis is mutually perpendicular to the a and c axes, the points of the first, second, third, etc., layer lines all coincide with those of the zero layer line. In other cases such as the monoclinic class, the points of the layer lines are shifted a distance corresponding to the angle β.

The indices of all points of the reciprocal lattice diagram are known, so that the indices of all possible reflecting planes in the crystal are known. The spacings of these planes may then be calculated by the equation (VIII). A comparison of the observed spacings with the calculated spacings leads to the identification of the reflecting planes. Then, by identifying those planes which ought, but which do not give a reflection, the space group may be determined.

It often happens that two or more sets of planes have almost the same spacing, and the resolving power of the apparatus is not great enough to separate the spots on a rotation photograph. It then becomes necessary to use the method in which a single crystal is oscillated through a small angle. When there is a

large number of reflecting planes, it is usually best to make a complete set of oscillation photographs. The crystal is set up as in the complete rotation method, with a crystallographic axis as the axis of rotation, and the incident beam of X-rays parallel to another known crystallographic axis. The crystal is then oscillated through a small angle, say 15°.A series of photographs is made,,one for the oscillation from 0° - 15°, one for 15° - 30°, and so on. This is repeated with each axis in turn as axis of oscillation, and is usually found sufficient to identify all the reflecting planes without any ambiguity.

In the projection of the reciprocal lattice normally on the equatorial plane, we get a reflection whenever a point in the projection intersects the projection of the circle of section of the sphere of reflection by a plane through the point parallel to the equatorial plane. (see figure 9). To find the indices of the planes which reflect during oscillation through a small angle, it is only necessary to rotate such circles about the pole of the axis through the angle of oscillation, noting the indices of the points which intersect the corresponding circles. When the axis of oscillation is a principal crystallographic axis, the points of the reciprocal lattice lie in planes parallel to the equatorial plane. There is therefore only one circle of section corresponding to all the spots in that layer line of the photograph.

The reciprocal lattice diagram is first constructed as before, and a circle of unit radius is described

about the origin.

Consider as before, a crystal rotating about the b axis, and that in the zero position the X-rays are parallel to the a axis. The crystal is oscillated through an angle of 15° at a time, 0° being the position when the X-rays are parallel to the a axis. On the circle of unit radius already described about the origin as centre, points whose angular positions correspond to the limits of oscillation, are marked off. In the case considered, the angular distance between these points is 15°, and they are measured from the a* axis. These points form the centres of the circles of section, of which the radius is different for each layer line. The radius of the zero layer line circle of section is unity. The radius r of the circle of section for the nth. layer line is given by the expression

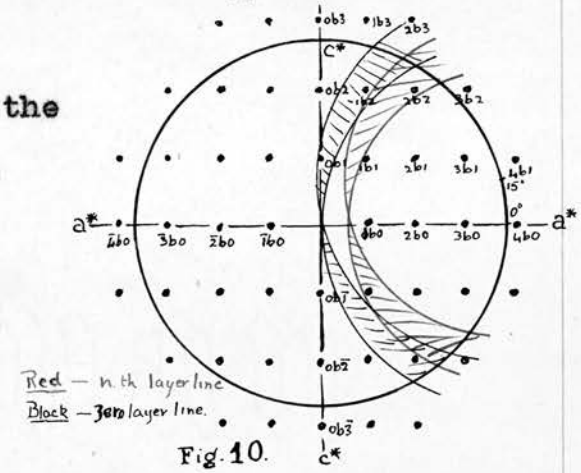


Fig. 10.

$$r^2 = 1 - n^2 b^{*2} \quad \ldots\ldots \text{(XI)}.$$

where the axis of oscillation is the b axis of the crystal. Circles of these radii are described about each of the centres, as shown in figure 10. Then, if in the two lunular spaces between the nth. and the (n 1)th. circles the points $h_1 l_1$, $h_2 l_2$ are found, then the planes (h_1, k, l_1), (h_2, k, l_2) will give reflections in the oscillation under consideration. Those points in one lune will reflect to the right, and those in the other lune to the left.

A point of the reciprocal lattice may be most conveniently referred to a cylindrical system of co-ordinates when dealing with rotation photographs. The axis of rotation is chosen as the axis, and the co-ordinates of any point in the reciprocal lattice are given as ξ, ζ, ω, (corresponding to the usual u, z, ϕ). The angular co-ordinate ω is indeterminate when dealing with complete rotations, and does not require to be considered here.

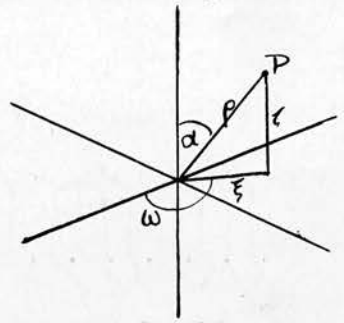


Fig.11.

It will be seen from figure 11 that the radius vector ρ is given by

$$\rho^2 = \xi^2 + \zeta^2$$

Combining this with equation (X) we obtain a relationship giving the glancing angle θ in terms of ξ and ζ

$$\sin\theta = \lambda/2d = \rho/2 = (\xi^2+\zeta^2)^{\frac{1}{2}}/2 \quad \ldots \text{(XII)}.$$

The angle α between the normal to the reflecting plane and the axis of rotation is given by

$$\tan\alpha = \zeta/\xi \quad \ldots\ldots\ldots \text{(XIII)}.$$

J. D. Bernal (loc. cit. page 15) gives charts of ξ and ζ from which the co-ordinates of any point in a rotation photograph may be read off directly. Thus if these co-ordinates are known the spacing of any set of planes may be calculated by means of the equation

$$d = \lambda/(\xi^2+\zeta^2)^{\frac{1}{2}} \quad \ldots\ldots \text{(XIV)}.$$

If a principal crystallographic axis be chosen as the axis of rotation, the spots of the photograph lie on layer lines of equal ζ. By measuring the values of ζ for these lines, the length of the primitive

translation may be determined from

$$a = n\lambda/\zeta \quad \ldots\ldots \text{(XV)}.$$

where the nth. layer line is under discussion. Hence the dimensions of the unit cell may be found.

Calculation of the theoretical values of ξ and ζ may be made from the equations

$$\xi = \lambda (k^2/b^2 + l^2/c^2)^{\frac{1}{2}} \quad \text{(XVI)}$$

and

$$\zeta = \lambda h/a \quad \ldots\ldots \text{(XVII)}.$$

where the crystal is rotated about the a axis. The equations refer to crystals belonging to the rhombic system. Identification of the space group to which the crystal belongs may then be carried out as has already been described.

EXPERIMENTAL PROCEDURE.

A description of the apparatus and of the details of experimental procedure is given here since such details apply generally to the work which has been carried out.

A diagramatic sketch of the X-ray tube and the vacuum system is given in figure 12 (page 23). A Shearer self-rectifying X-ray tube was used to generate the X-rays. The anode B was a short length of brass tubing which had a water cooling system. The anti-cathode A was placed opposite a small window of thin aluminium foil F, which allowed the X-rays to pass through. An air-tight joint was obtained here by means of wax which was also used to seal the glass tube E to the anode and cathode ends of the X-ray tube.

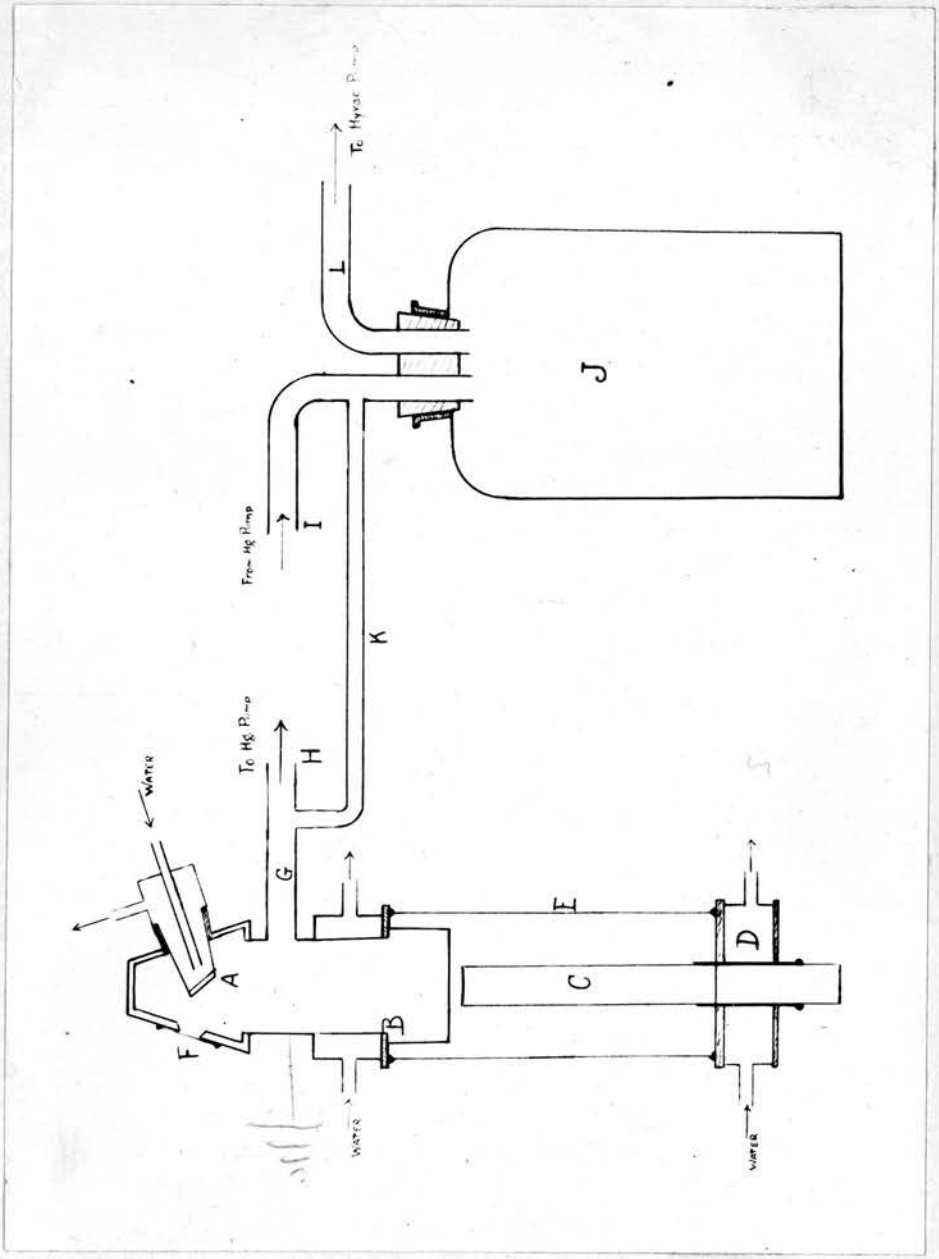

To Hyvac Pump
L
J
From Hg Pump
I
K
To Hg Pump
H
WATER
G
A
F
E
D
C
B
WATER
WATER

Figure 12.

The cathode C was a length of aluminium rod which passed through a cooling chamber D along the central axis of the tube to within a short distance of the anti-cathode. The end of the cathode facing the anti-cathode was turned to a concave shape in order to focus the stream of electrons on to the centre of the anti-cathode. The radius of curvature was made equal to the distance of the cathode from the anti-cathode, the greatest intensity of the X-ray beam being thus obtained.

The X-ray tube was exhausted through the tube G by means of a two stage Gaede steel mercury diffusion pump, the outlet I of which was connected to a large bottle J of about two litres capacity. The bottle acted as a reservoir and was exhausted by means of a "Hyvac" oil pump. In order to maintain a constant pressure within the X-ray tube a leak back from the reservoir was provided in the tube K. Once the vacuum required for the generation of X-rays had been attained the volume of gas allowed to pass back into the X-ray tube through the tube K was adjusted to equal that withdrawn by the mercury pump.

The necessary high tension current was obtained from the secondary winding of a transformer working off the A.C. power mains. The current passing through the primary winding of the transformer was regulated by means of a resistance so that a current of approximately 10 milliamperes was passed through the X-ray tube at a pressure of about 60,000 volts. The cathode of the X-ray tube was connected to one terminal of the secondary winding while the other terminal of

this winding was connected to earth. The anode end of the X-ray tube was also earthed, and was cooled by passing a stream of water from the water main through the cooling system. The earthing of the anode and of one terminal of the transformer secondary decreased the danger of working with such a high tension current, since only the cathode end of the X-ray tube was then "live".

In order to prevent the possibility of sparking inside the X-ray tube a small spark gap was connected in parallel with the tube. The width of the gap was adjusted so that when the vacuum in the tube became harder than was required for the production of the most intense X-rays, the high tension current jumped across the spark gap instead of inside the X-ray tube. The gap was found to work best when the balls were from 3 to 4 centimeters apart.

When all adjustments had been made it was possible to run the X-ray tube for long periods without more attention than a slight adjustment of the screw clips controlling the leak back from the reservoir to the X-ray tube.

A Muller X-ray spectrograph was used in the work, and since there was no cylindrical camera, one was designed to suit the instrument. The design is shown in figure 13. A small goniometer was used with the camera for setting the crystal in the required position, the arcs of the goniometer being capable of a setting over about 25°. The camera was constructed with a

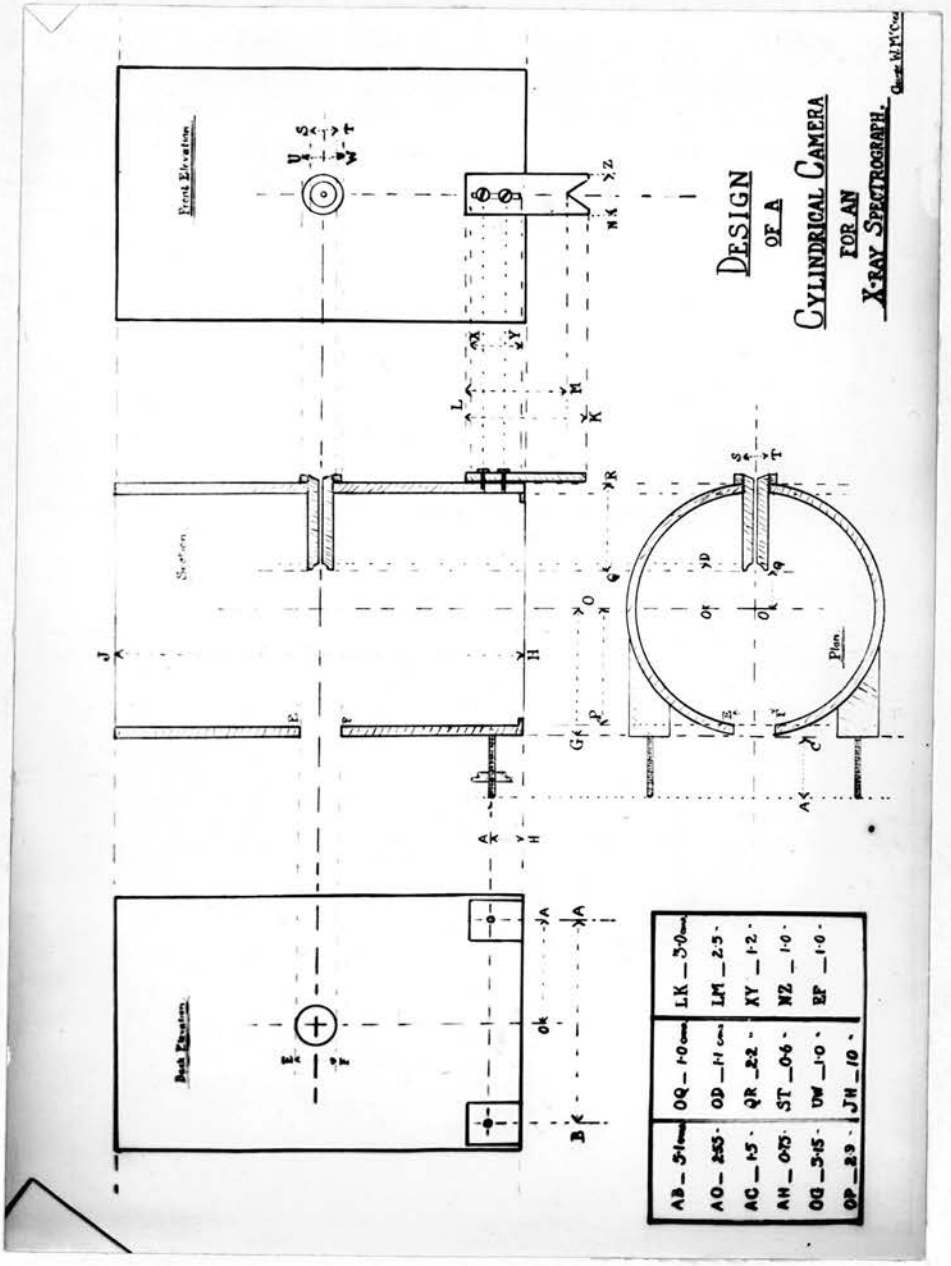

DESIGN
OF A
CYLINDRICAL CAMERA
FOR AN
X-RAY SPECTROGRAPH.
Front Elevation
Back Elevation
Section
Plan
AB — 5·1 mm
AO — 2·83 ·
AC — 1·5 ·
AH — 0·75 ·
OG — 3·45 ·
OP — 2·3 ·
OQ — 1·0 mm
OD — 1·1 cm
QR — 2·2 ·
ST — 0·6 ·
UW — 1·0 ·
JH — 1·0 ·
LK — 3·0 mm
LM — 2·5 ·
XY — 1·2 ·
MZ — 1·0 ·
EF — 1·0 ·

Figure 13.

diameter such that the diameter of the film when inside of the camera was 5·73 cms. Such a diameter simplifies the calculation of the results, since a distance of 1 millimeter measured along the zero layer line of the unrolled film was equivalent to 2° of arc.

The crystal employed in the experiments was small and was examined under a microscope in order to ascertain if it were free from striations and other imperfections. A good crystal was attached to the end of a fine glass fibre by a trace of shellac or liquid glue. The crystal was then easily handled. The free end of the glass fibre was then attached to the goniometer and the crystal was first set in the required position by viewing through a microscope.

The accurate setting of a crystal belonging to the ortho-rhombic system is most easily done by means of X-rays. If such a crystal is set with say the $\underline{b}$ crystallographic axis as the axis of rotation, and in the initial position the X-ray beam is parallel to the $\underline{a}$ axis, a set of planes $(h,k,\underline{l})$ will be in a position to reflect X-rays of wavelength $\underline{\lambda}$, when the crystal is in the initial position. In the rhombic system of crystal symmetry sets of planes $(h,k,\underline{l})$, $(h,k,\underline{\bar{l}})$, $(h,\bar{k},\underline{l})$, and $(h,\bar{k},\underline{\bar{l}})$ having the same spacing will be in such a position as to reflect X-rays of wavelength $\underline{\lambda}$ at the same instant. Thus, if a Laue photograph is made when the crystal is in the initial position four spots will be found at equal distances from the centre of the plate. These spots are caused by reflections

of X-rays of wavelength λ by the set of planes (h,k,l). If the crystal is not set correctly, the four spots will not be equidistant from the centre of the photograph, and a method of setting the crystal then becomes apparent.

The crystal is first set approximately in the initial position by means of a microscope, and a Laue photograph is then made with the plate very close to the crystal, the position of which is noted on the goniometer scales. If the four spots corresponding to one set of planes are not equidistant from the centre of the photograph, another photograph is made with the crystal in a different setting. The positions of the spots in question are again noted, and on comparison of the two photographs, the correct setting of the crystal is made, this position being found by proportion. It is necessary to use only a small photographic plate or film for setting purposes, as the distance of the plate from the crystal need be only 1 centimeter. Small size Dental X-ray film was used in the setting of the crystals. When using a molybdenum anti-cathode and passing a current of 10 milliamperes at 60,000 volts through the X-ray tube, the exposure required in making Laue photographs for setting purposes was about half an hour, but this varied with the particular crystal in use.

Once the crystal was set in the desired position, complete rotation and oscillation photographs were made. The photographic film was enclosed in a thin, light-proof, black paper envelope which was then bent round

inside the cylindrical camera, and held in position by by two spring clips. The camera was then placed on the spectrometer, and the crystal rotated at a constant speed by a clock-work motor on the instrument. X-rays from a copper anti-cathode were passed through the slit of the camera whence they fall on the crystal at a point on the axis of rotation, and the X-ray beam is then reflected by the planes within the crystal, the reflections being recorded on the photographic film. It was not necessary to filter the X-rays since it was easily possible to separate the spots on the photograph caused by reflection of the K_α rays from those caused by reflection of the K_β rays, owing to the difference in position on the photograph and to the difference in intensity of the reflections. The exposure required to give a good photograph was about four hours, but an exposure of five hours was given in order that faint spots might be more easily detected.

In making an oscillation photograph, the crystal was set as before, but the clock-work mechanism was arranged to oscillate the goniometer by means of a cam and arm instead of rotating the goniometer. The initial position of the crystal was taken as the position of 0° in the oscillation, and the oscillation was made from this position as zero.

The dimensions of the unit cell were first determined from the photographs by measurement of the ζ co-ordinate of each spot, by means of the Bernal chart referred to on page 21. The results of these measurements

were confirmed by measurement of the distance of each layer line from the zero layer line by means of a steel rule, and the subsequent calculation of the primitive translations by means of the equations (I) and (II). The ξ co-ordinate of each spot was then found from the Bernal chart.

A set of six oscillation photographs was made with each of the three axes in turn as the axis of oscillation, the oscillation in each case being 15°. As the initial position of the crystal was known, the co-ordinate ω was known and hence the crystal planes which came into the reflecting position during a given oscillation could be determined from a reciprocal lattice diagram. It was found that an oscillation of 15° was sufficient to separate all the reflections from planes of nearly equal spacing, when such reflections were indistinguishable on rotation photographs.

Calculation of the spacing of each plane was made from the observed values of ξ and ζ (equation XIV). These spacings are referred to as the observed spacings. A further calculation of the spacings was made from equation (VIII), and these values are referred to as the calculated spacings.

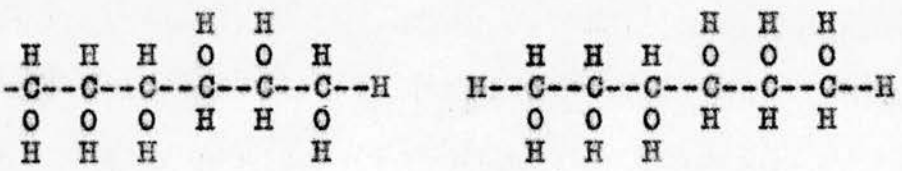
The number of planes which came into the reflecting position, and their indices, was determined from reciprocal lattice diagrams constructed from the values of $\underline{a}$, $\underline{b}$, and $\underline{c}$ which were obtained from the rotation photographs. A comparison of the observed and calculated spacings will then show any abnormal spacings. The space group to which the crystal belongs may then be determined.

E X P E R I M E N T A L .

d - M A N N I T O L.

Mannitol, $C_6H_{14}O_6$, exists in three modifications, a dextro-rotatory and laevo-rotatory form and an inactive variety. The dextro- form occurs frequently in plants and is so named because of its occurence in the manna ash (fraxinus ornus), the dried sap of which is manna. The d-mannitol is obtained from this source by extraction with alcohol and allowing the substance to crystallise out. It is also prepared in the ropy fermentation of the different varieties of sugar, and may be prepared together with sorbitol, by the action of sodium amalgam on d-mannose and on d-fructose.

The structure of d-mannitol has been worked out by chemical means and shows two possible configurations for the molecule.



(I) (II)

Numbering the carbon atoms from left to right 1 to 6, it will be seen that the hydroxyl group attached to carbon atom 6 has a choice of two positions as shown in formula (I) and (II). It was believed that this hydroxyl group was free to rotate and thus had no fixed position. Irvine and Paterson (J.C.S., 1914, 105, page 898) studied the iso-propylidene derivatives and the methylated hexitols derived from them, and have found that the terminal primary hydroxyl groups in the

d-mannitol molecule do not appear to possess free rotation, but assume preferentially a fixed position. These positions are shown in formula (I).

Although d-mannitol possesses a configuration which is apparently symmetrical, the terminal hydroxyl groups are differently arranged, and thus affect the reactions of the compound. It is usually believed that a di-derivative of d-mannitol, involving the hydroxyl groups attached to the carbon atoms 1 and 2, would be identical with the derivative in which the hydroxyl groups attached to the carbon atoms 5 and 6 were similarly substituted. It is possible that such would not be the case, but so far no isomeric pair of compounds of this nature has been prepared.

A comparison of the reactive powers of the hydroxyl groups attached to carbon atoms 1, 2, and 5, 6 by physical methods (Irvine and Steele, J.C.S., 1915, 107, page 1221) has shown that there is a difference in the respective reactive powers. The results show that while the hydroxyl groups in the pairs 5,6, and 3,4 behave as if they were thrust apart, the groups in the pair 1,2 must lie in proximity. This is in strict agreement with the structure of d-mannitol shown in formula (I), which has been accepted as the formula of d-mannitol.

When crystallised from alcohol, d-mannitol is obtained in the form of delicate needles. From water it crystallises in large rhombic prisms which have been described by Groth (Chemische Krystallographie, III, p. 431).

α-Modification

Rhombic bisphenoidal,

a:b:c = 0·4718:1:0·5200 (Schabus)

β-Modification

Rhombic bisphenoidal,

a:b:c = 0·5121:1:0·6577 (Zepharovich)

The two forms are stated to have the same melting point (166°C), and to have the same chemical properties. Although they are alike in solution, no conversion of the one form to the other takes place. The two forms differ in the axial ratios and in the faces which are developed in the crystals.

Commercial d-mannitol is the β-modification, which is always obtained in a crystallisation from water or alcohol.

Becker and Rose (Zeit. fur PhysiK, 14, 369, 23) give results of an X-ray examination of d,l-mannitol in which they found the lengths of the axes a, b, and c to be 10·36, 8·1, and 4·55 A.U. respectively, and that there were 2 molecules in the unit cell. The calculated density of the crystal was found to be 1·55 gms/cc. the value given in the International Critical Tables being 1·521. The space group to which the crystal belongs is not mentioned and no attempt is made to obtain a structure for the molecule of the inactive mannitol used.

Crystals of d-mannitol were obtained for the work, the results of which are now to be given, by

recrystallising pure commercial d-mannitol twice from water. The crystals used in making the photographs were chosen after examination under the microscope, and were free from twinning and striations. Three crystals were used in all; one crystal was set with the a axis, another with the b axis, and the third with the c axis as the axis of rotation. In each case the crystal was attached to a fine glass fibre by means of a quick-hardening glue, the fibre then being fixed to the goniometer by plasticine.

The crystals were small, about 1·0 x 0·5 x 1·0 mm. and were assumed to be of the same degree of purity as the samples which were tested for melting point and optical rotation.

The melting points of the three forms of mannitol are given by Richter (Organic Chemistry vol. I, page 623) as d-mannitol - 166°C, l-mannitol - 163-164°C, and d,l-mannitol - 168°C. The observed melting point was 166°C.

In solution in water d-mannitol shows a very small optical rotation of −0·25°, but in a 5% borax solution the optical rotation is given as +22·5° (J.E. McKenzie, Sugars and their Simple Derivatives, page 166). The observed rotation was +22·2° in a 5% borax solution.

These results show that the substance examined was d-mannitol, and the method of crystallisation would then yield the β-modification.

Several rotation photographs were made with each of the principal crystallographic axes in turn as the

axis of rotation, and the dimensions of the unit cell were obtained from measurements made on these photographs.

On none of the photographs was it possible to find traces of spots lying between the well-marked layer lines, even when the film was given a very long exposure (15 hours). The sizes of the sides of the unit cell were then taken as the average values calculated from the layer lines of each photograph.

Table I on page 36 shows the dimensions of the unit cell as they were obtained from the photographs.

The reciprocal lattice diagrams shown in figures 14, 15, and 16 (pages 37, 38, 39) were then constructed from the observed values of the primitive translations where

$$a^* = \lambda/a = 0{\cdot}1776$$

$$b^* = \lambda/b = 0{\cdot}0929$$

$$c^* = \lambda/c = 0{\cdot}2798$$

From these diagrams the indices of all the crystal planes which came into the reflecting position during either a complete rotation or an oscillation of the crystal, were obtained.

Assuming a definite number of molecules in the unit cell, the spacing $\underline{d}$ of any plane having the indices $(h,k,\underline{l})$ may be calculated by means of the equations

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{\underline{l}^2}{c^2} \quad \ldots\ldots \text{(IV)}.$$

and $$abc\rho = \text{N.M. } 1{\cdot}65 \quad \ldots\ldots \text{(VII)}.$$

combining to give

$$d = \frac{\text{N.M. } 1{\cdot}65}{\rho\sqrt{(h^2b^2c^2 + k^2a^2c^2 + \underline{l}^2a^2b^2)}} \quad \ldots \text{(VIII)}.$$

T A B L E (I).

Rotation about the a axis.

	1st layer line.	2nd layer line.	3rd layer line.	4th layer line.
Average length of a axis.	8.661	8.660	8.670	8.667

Length of the a axis is 8.664 A.U.

Rotation about the b axis.

	1st layer line.	2nd layer line.	3rd layer line.	4th layer line.
Average length of b axis.	16.43	16.34	16.67	16.48

	5th layer line.	6th layer line.	7th layer line.	8th layer line.
Average length of b axis.	16.69	16.73	16.59	16.73

Length of the b axis is 16.58 A.U.

Rotation about the c axis.

	1st layer line.	2nd layer line.
Average length of c axis.	5.498	5.504

Length of the c axis is 5.501 A.U.

Length of the a axis is . . . . . 8.664 A.U.

Length of the b axis is . . . . . 16.58 A.U.

Length of the c axis is . . . . . 5.501 A.U.

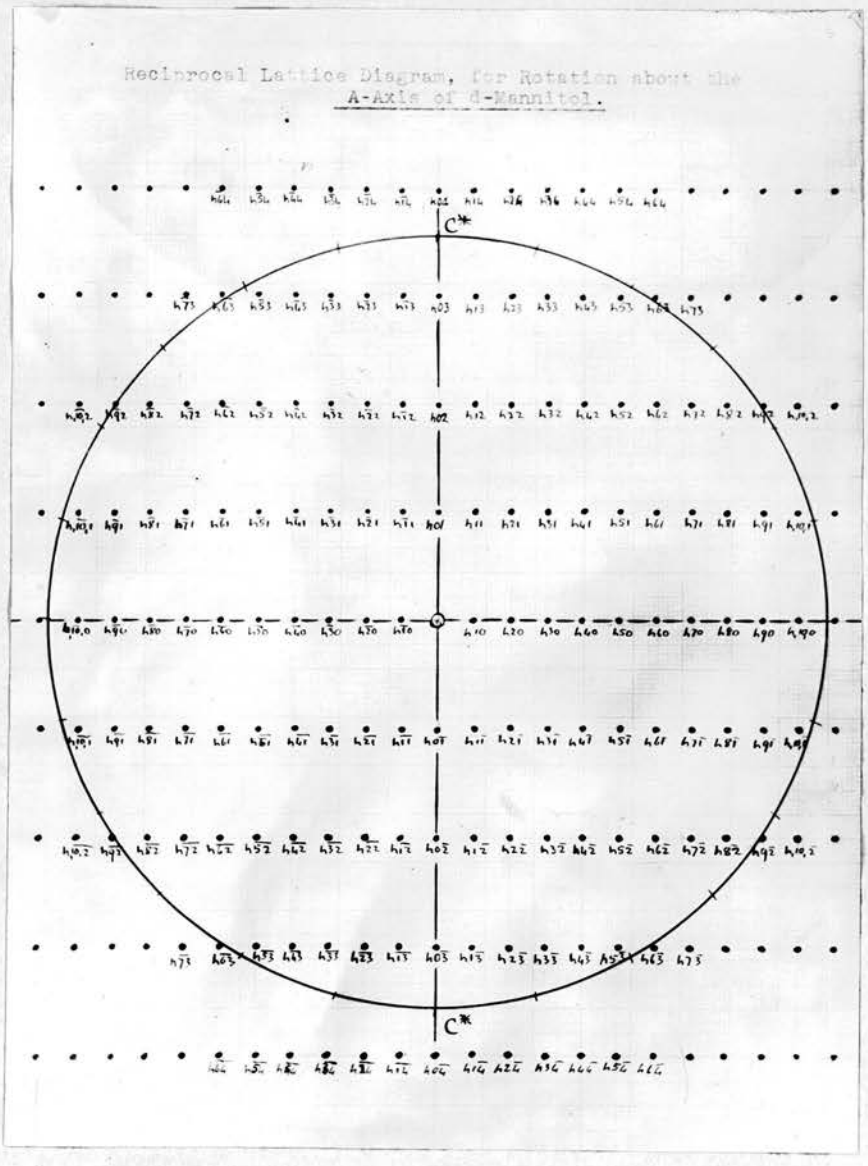

Reciprocal Lattice Diagram, for Rotation about the
A-Axis of d-Mannitol.
C*
C*

figure 14.

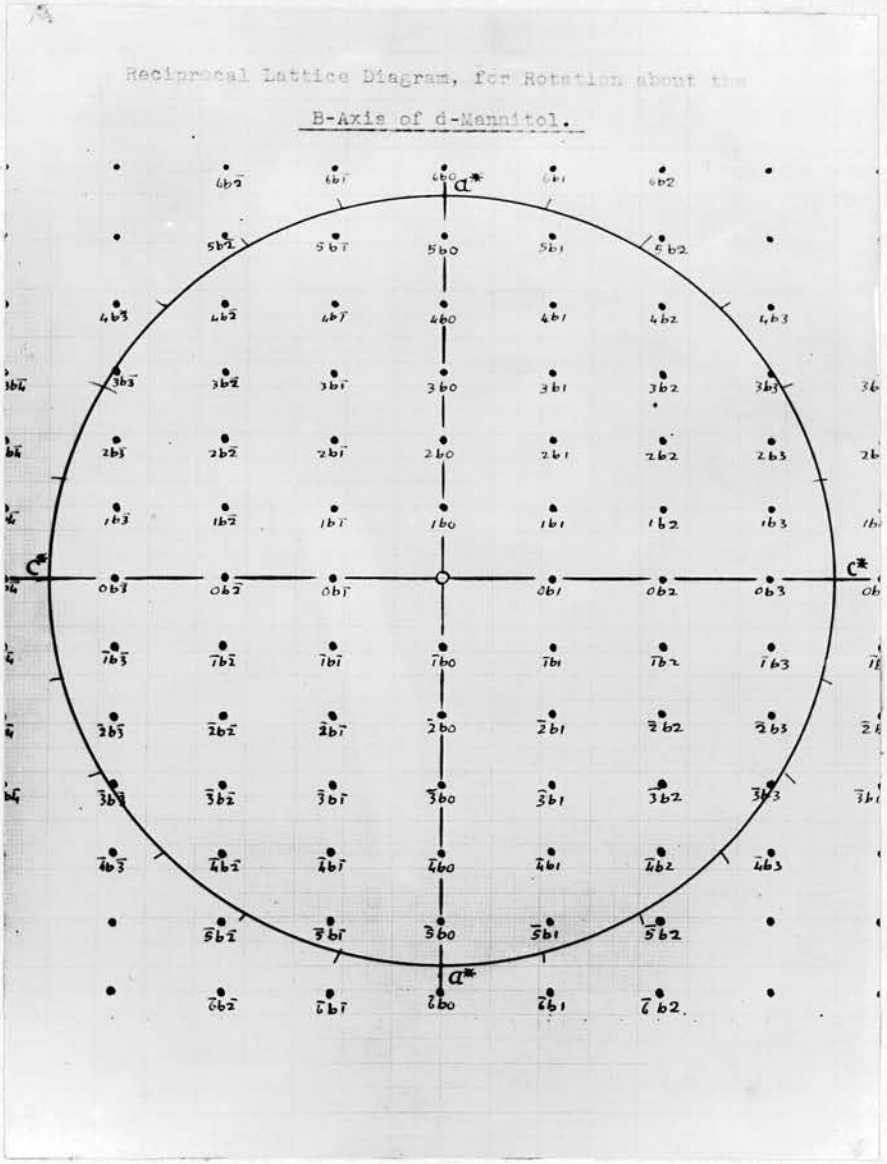

Reciprocal Lattice Diagram, for Rotation about the
B-Axis of d-Mannitol.
a*
a*
c*
c*

Figure 15.

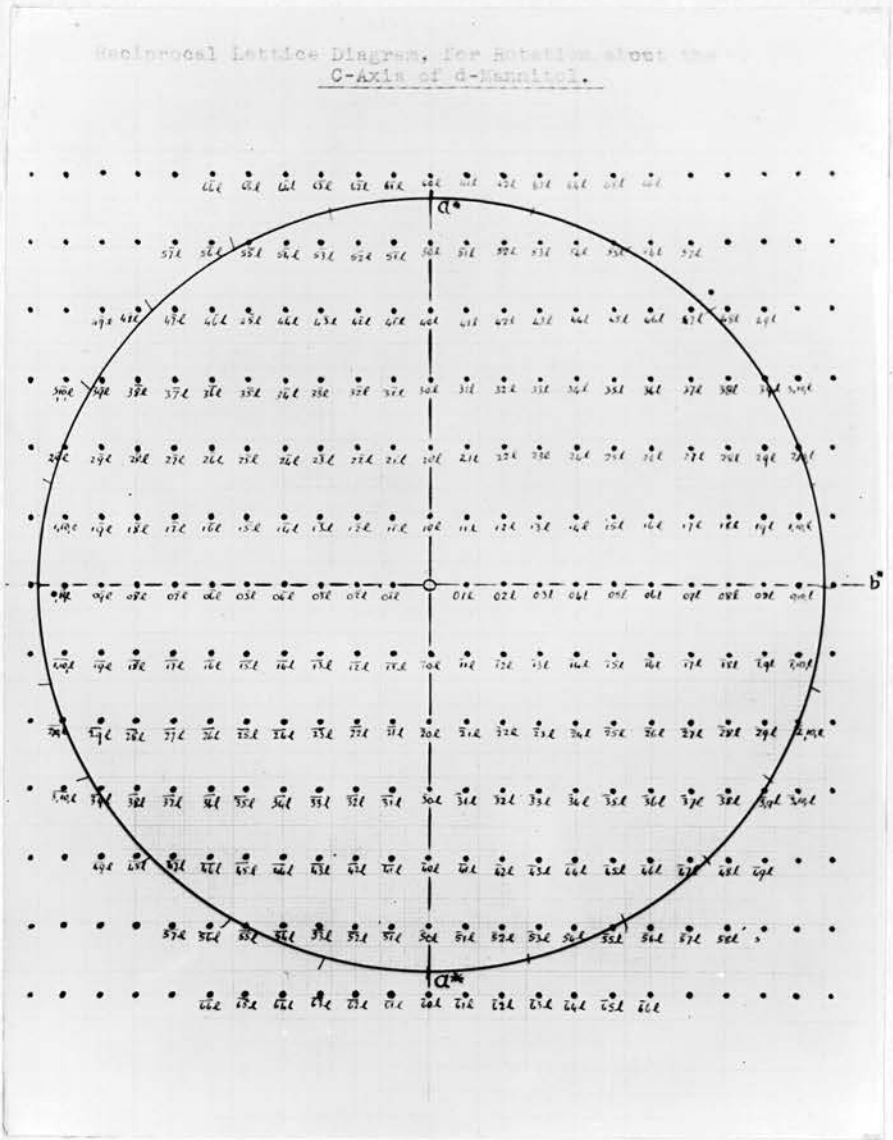

Reciprocal Lattice Diagram, for Rotation about the
C-Axis of d-Mannitol.
c*
b*
a*

Figure 16.

It was assumed that there were four molecules in the unit cell of the d-mannitol crystal, and the density ρ of the crystal, calculated from the equation (VII), was then found to be 1·522 gms./cc., that ascertained from actual experiment and recorded in the International Critical Tables being 1·521 gms./cc.

Since the density of the crystal calculated from the X-ray data on the assumption that there were four molecules in the unit cell gives a value which agrees very closely with the experimental result, the assumption that there were four molecules in the unit cell is justified.

Calculation of the spacings of all reflecting planes was then made by means of equation (VIII), these spacings being given in the second column of Table II (pages 41 to 43) under the heading of "Calculated Spacings". The third column of this table gives the spacings of the planes whose reflections were recorded on the photographic films. These spacings which were calculated from the $\underline{\xi}$ and $\underline{\zeta}$ co-ordinates of the spots on the photographs by means of equation (XV), are the "Observed Spacings".

In all, reflections from nearly two hundred sets of crystal planes were observed, and the planes identified.

It will be seen from Table II that

(A) the odd order reflections from the (100), (010) and (001) planes are absent, i.e. the spacings of these planes is halved,

(B) no doublings or halvings of the spacings of any other planes were found,

(C) the reflections from seven planes were so faint that the spot corresponding to the reflection was

TABLE (II).

Plane Indices	Calc. Spacing	Obs. Spacing	Plane Indices	Calc. Spacing	Obs. Spacing
100	8.680		500	1.736	
110	7.690	7.675	510	1.727	1.702
120	5.997	5.985	520	1.707	1.697
130	4.661	4.594	530	1.654	1.650
140	3.740	3.697	540	1.601	1.595
150	3.098	3.062	550	1.538	1.529
160	2.633	2.612	560	1.470	1.463
170	2.285	2.265	570	1.400	1.392
180	2.016	2.005	580	1.331	1.317
190	1.802	1.793			
1100	1.629	1.614	001	5.509	
			101	4.652	4.654
200	4.340	4.210	201	3.409	3.407
210	4.199	4.192	301	2.562	2.559
220	3.843	3.838	401	2.019	2.016
230	3.412	3.384	501	1.656	1.653
240	2.997	2.971			
250	2.635	2.609	002	2.756	2.754
260	2.331	2.310	102	2.628	2.624
270	2.079	2.058	202	2.327	2.324
280	1.871	1.879	302	1.996	1.993
290	1.696	1.683	402	1.706	1.703
2100	1.549	1.535			
			003	1.837	
300	2.893		103	1.797	1.792
310	2.880	2.843	203	1.692	1.687
320	2.732	2.727	303	1.551	1.540
330	2.563	2.549	403	1.402	
340	2.373	2.358			
350	2.180	2.160	010	16.58	
360	1.998	1.983	011	5.230	5.219
370	1.833	1.818	012	2.718	2.714
380	1.685	1.675	013	1.826	1.823
390	1.554	1.558			
3100	1.439	1.427	020	8.289	8.273
			021	4.590	4.579
400	2.170	2.111	022	2.615	2.613
410	2.152	2.148	023	1.793	1.789
420	2.099	2.096			
430	2.020	2.011	030	5.529	
440	1.923	1.896	031	3.903	3.896
450	1.816	1.791	032	2.467	2.460
460	1.707	1.679	033	2.744	1.739
470	1.600	1.577			
480	1.499	1.486	040	4.145	4.136
490	1.405	1.397	041	3.310	3.274
4100	1.318	1.304	042	2.295	2.290
			043	1.680	1.682

Plane Indices	Calc. Spacing	Obs. Spacing
050	3.317	
051	2.842	
052	2.120	2.108
053	1.608	1.601
060	2.764	2.763
061	2.471	2.450
063	1.530	1.525
062	1.952	1.942
070	2.369	
071	2.177	2.159
072	1.796	1.786
073	1.419	1.446
080	2.073	2.072
081	1.941	1.931
082	1.657	1.649
083	1.375	
090	1.842	
091	1.748	1.741
092	1.532	1.530
0100	1.658	1.655
0101	1.588	1.574
0102	1.421	1.430
111	4.480	4.455
112	2.594	2.585
113	1.787	1.781
121	4.057	4.035
122	2.504	2.497
123	1.757	1.751
131	3.560	3.530
132	2.373	2.333
133	1.690	1.703
141	3.095	3.070
142	2.219	2.209
143	1.649	1.644
151	2.700	2.673
152	2.059	2.044
153	1.580	1.573
161	2.280	2.257
162	1.904	1.894
163	1.507	1.499
171	2.111	2.095
172	1.759	1.748
173	1.452	

Plane Indices	Calc. Spacing	Obs. Spacing
181	1.894	1.877
182	1.625	1.616
191	1.713	1.700
192	1.509	1.497
1101	1.562	1.549
1102	1.402	1.393
211	3.341	3.312
212	2.305	2.290
213	1.683	1.675
221	3.154	3.113
222	2.240	2.227
223	1.658	1.649
231	2.902	2.875
232	2.145	2.129
233	1.618	1.609
241	2.633	2.603
242	2.029	2.017
243	1.566	1.559
251	2.378	2.356
252	1.905	1.893
253	1.511	1.499
261	2.147	2.129
262	1.780	1.765
263	1.443	
271	1.946	1.926
272	1.660	1.649
273	1.377	
281	1.771	1.756
282	1.548	1.535
283	1.311	
291	1.621	1.603
292	1.444	1.431
2101	1.491	1.479
2102	1.350	1.337
311	2.532	2.491
312	1.981	1.962
313	1.543	1.535
321	2.448	2.416
322	1.940	1.921
323	1.507	1.513
331	2.325	2.290
332	1.877	1.860

Plane	Calc. Spacing	Obs. Spacing	Plane	Calc. Spacing	Obs. Spacing
341	2.179	2.147	481	1.446	1.433
342	1.798	1.783	482	1.317	1.301
343	1.453	1.445			
			491	1.361	1.345
351	1.998	2.002			
352	1.710	1.687	4101	1.282	1.269
353	1.405	1.395			
			511	1.648	1.622
361	1.878	1.859	512	1.463	1.447
362	1.618	1.607			
363	1.353	1.352	521	1.624	1.598
			522	1.447	1.431
371	1.760	1.720			
372	1.526	1.513	531	1.586	1.564
373	1.296	1.285	532	1.420	1.407
381	1.612	1.593	541	1.538	1.500
382	1.438	1.424	542	1.382	1.372
383	1.241	1.233			
			551	1.481	1.464
391	1.496	1.481			
			561	1.421	1.405
3101	1.400	1.380			
			571	1.357	1.343
411	2.005	1.972			
412	1.716	1.673	581	1.294	1.282
413	1.397	1.386			
421	1.962	1.935			
422	1.670	1.670			
423	1.383	1.375			
431	1.897	1.872			
432	1.629	1.612			
433	1.359	1.337			
441	1.815	1.788			
442	1.577	1.557			
443	1.328	1.320			
451	1.725	1.703			
452	1.517	1.505			
453	1.292	1.285			
461	1.630	1.607			
462	1.451	1.438			
471	1.537	1.516			
472	1.384	1.367			

not observed on the photographic film.

The only abnormal spacings observed were those of the (1,0,0), (0,1,0), and (0,0,1) planes whose spacings were halved. There are therefore four molecules in the unit cell.

Reference to the tabulated data given by W.T. Astbury and K. Yardley (Phil. Trans. Roy. Soc., A, ccxxiv, page 221) shows that for a crystal belonging to the rhombic bisphenoidal class, and for which the (1,0,0), (0,1,0) and (0,0,1) planes show a halved spacing, the Bravais lattice is the simple lattice Γ_0, and the space-group is Q^4.

The correct axial ratio is then

$$a:b:c = 0{\cdot}5225:1:0{\cdot}3319.$$

Groth's value of the axial ratio was given as

$$a:b:c = 0{\cdot}5121:1:0{\cdot}6577$$

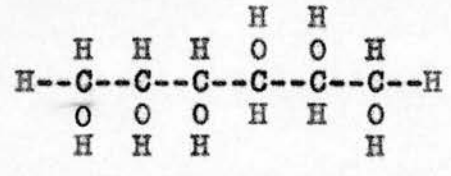
showing that the c axis of the true unit cell is approximately half the value obtained from the crystallographic data.

The X-ray analysis has shown that there are four molecules in the unit cell of the d-mannitol crystal, and since the crystal belongs to the space-group Q^4, these molecules must be asymmetric (Astbury and Yardley, loc. cit.). The crystal molecules have the same molecular weight as the chemical molecules of d-mannitol.

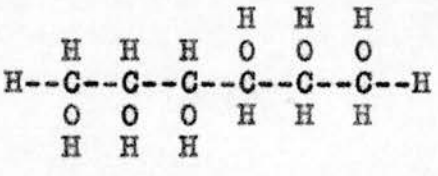
Further, in every case of the orthorhombic system so far investigated, the unit cell appears to contain the minimum number of molecules instead of an integral multiple of that number. (Astbury and Yardley, loc. cit.).

Each crystal molecule may therefore be expected to consist of only one chemical molecule. Hence the chemical molecule must be asymmetric.

An examination of the symmetry properties of the two possible configurations of the d-mannitol molecule shows that formula I is asymmetric, while formula II possesses a diad axis of symmetry.



(I).



(II).

The configuration of the chemical molecule of d-mannitol is therefore represented by formula I, which Irvine and his co-workers have shown to be the configuration of d-mannitol in solution.

The construction of a model of the d-mannitol molecule has made it clear that the arrangement of the atoms in space in such a way as to correspond to formula I, yields a configuration which is asymmetric.

The results given in Table I (page 36) show, on examination, that the length of the b axis calculated from the first, second, sixth, and eighth layer lines differs from the mean value by a relatively large amount. In the rotation photographs of the b axis, the distance of the first and second layer lines from the zero layer line is so small that a small error in the measurement of this distance introduces a relatively large error in the calculation of the spacing. The spots belonging to the higher order layer lines are

faint owing to the reflected ray having to travel a greater distance than in the case of the lower order layer lines. Since the reflected ray of the higher order layer lines must strike the photographic film obliquely, the spots become elongated. Both of these factors increase the difficulty of obtaining accurately the centres of the spots. This introduces a possible error in the measurement of the distance of the layer line from the zero layer line, and thus a corresponding error in the length of the axis calculated from this measurement. The amount by which the length of the b axis differs from the mean value when calculated from the layer lines noted above thus lies within the limits of experimental error.

SUMMARY.

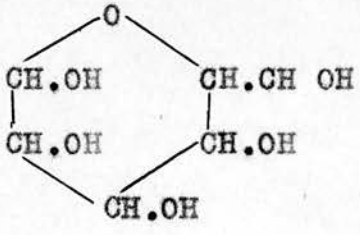
The results of the X-ray analysis of d-mannitol show that the lengths of the sides of the unit cell of the crystal are a = 8.664 A.U., b = 16.58 A.U., c = 5.501 A.U. There are 4 molecules in the unit cell, and the calculated density is 1.522 gms./c.c. The Bravais lattice is the simple lattice Γ_o, and the space-group is Q^4. The structure of the molecule of d-mannitol in the crystal has been found to be that deduced by Irvine and his collaborators for the substance when in solution.

d - M A N N O S E.

d-Mannose, $C_6H_{12}O_6$, is an aldohexose which is produced by the careful oxidation of the hexahydric alcohol d-mannitol. d-Mannose is a white hygroscopic compound which can be converted into d-glucose from which it differs only in the relative arrangement of the groups attached to the carbon atom adjacent to the aldehyde group.

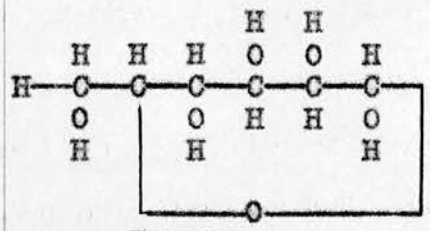
The structure of d-mannose is still the subject of discussion, but it is generally acknowledged that a ring structure is present in the molecule.

There are three different forms of this sugar known to chemists, α-, β-, and a labile or γ- d-mannose. The three forms differ in their internal arrangement, Goodyear and Haworth (Jour. Chem. Soc., 1927, II, p. 3136) stating that the normal or α- and β- forms of the sugar have a pyran ring structure, while the labile form has a furan ring structure. The normal sugar is therefore a tetrahydroxy-tetrahydro-pyran or mannopyranose

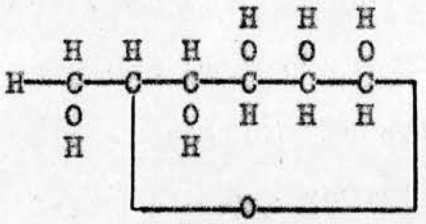


In order to explain the difference between the α- and β- forms of d-mannose Haworth and Hirst (Jour. Chem. Soc., 1928, I, p. 1221) make use of a possible cis- and trans- arrangement in which the hydroxyl groups attached to the first and second carbon atoms are affected. In equilibrium mixtures of the two forms

there is a tendency for the trans- form to predominate The structures of the two forms are thus:-



Trans-
α-d-mannose.



Cis-
β-d-mannose.

Further proof of the structure of d-mannose has been obtained by H.S. Isbell (Bur. Stand. J. Res., 1930, 5, p. 1179) who has shown that the epimeric difference in the molecular rotation between 4-glucosido-α-mannose and cellobiose approximates to the difference of that between α-d-mannose and α-d-glucose. This suggests that the ring structures of α-d-mannose and 4-glucosido-α-mannose are identical. This result is directly opposed to the work of Hudson and others, but supports Haworth's view that no change occurs in the ring structure of mannose during methylation.

Moreover, it has been proved by Haworth and others (Jour. Chem. Soc., 1930, p. 2664) that 4-glucosido-α-methyl mannoside contains a pyran ring structure. It would therefore appear that the most probable structure for the d-mannose molecule is that containing a pyran ring. Haworth's explanation of the two forms of d-mannose is then probably correct.

Owing to the fact that d-mannose is hygroscopic it is only with difficulty that crystals of any size may be prepared. A method of obtaining good crystals was suggested by Sir James Irvine in a private communication

A hot saturated solution of d-mannose in water was flooded with three to four times its volume of boiling glacial acetic acid. On standing, crystals of d-mannose separated out and were filtered off. Any acetic acid which might adhere to the crystals was removed by washing with dry acetone. Prepared in this way d-mannose is not hygroscopic, but the crystals are not very permanent, becoming opaque after some time.

P.A. Levene (J. Biol. Chem., 1924, 59, p. 129) describes a method of preparing α-d-mannose which is very similar to that given above. 100 gms. of d-mannose are dissolved in 25ccs. of water and cooled to 0°C. 400 ccs. of cooled glacial acetic acid are added and crystals of α-d-mannose separate out and are filtered after four or five hours, and subsequently extracted with alcohol.

The similarity of the methods makes it appear probable that crystals of α-d-mannose were used in this X-ray analysis.

Since only a few crystals were obtained it was not possible to test their purity by means of the optical rotation of a solution. A determination of the melting point was made and the crystals were found to melt at 132 - 132·5°C. Groth (Chem. Kryst., vol. III, p. 441) gives the melting point of d-mannose as 132°C.

Groth (loc. cit.) describes only one form of d-mannose crystal, giving:-

Rhombic bisphenoidal;

$$a : b : c = 0.319 : 1 : 0.826 \quad \text{(Mohr)}$$

Single crystal rotation photographs were made, using each of the principal crystallographic axes in turn as the axis of rotation; the dimensions of the unit cell were obtained from measurements made on these photographs. The dimensions of the unit cell are given in Table III (page 51).

While the direction of the crystallographic axes is purely arbitrary, it is usual to name that axis which is parallel to the greatest length of the crystal the c axis. Such a procedure was adopted in the case of d-mannitol, and in the case of d-mannose. It will be seen from the results of Table III that the length of the c axis of d-mannose corresponds to that of the a axis of d-mannitol.

Adopting the dimensions of the unit cell given in Table III as the basis of calculation, it was found by means of equation (VII) (page 35), that there were 4 molecules in the unit cell, and that the calculated density of the crystal was then 1.602 gms./c.c., the value given in the International Critical Tables being 1.539 gms./c.c.

The sets of planes in the crystal which came into the reflecting position during a complete rotation of the crystal were determined from reciprocal lattice diagrams which are shown in figures 17, 18, and 19 (pages 52, 53, and 54). These diagrams were constructed from the observed values of the dimensions of the unit

T A B L E (III).

Rotation about the a axis.

	1st.layer line.	2nd layer line.	3rd layer line.	4th layer line.
Average length of a axis.	5.515	5.552	--	--

Length of the a axis is 5.533 A.U.

Rotation about the b axis.

	1st layer line.	2nd layer line.	3rd layer line.	4th layer line.
Average length of b axis.	17.77	17.87	17.56	17.62

	5th layer line.	6th layer line.	7th layer line.	8th layer line.
Average length of b axis.	17.53	17.67	17.56	--

Length of the b axis is 17.66 A.U.

Rotation about the c axis.

	1st layer line.	2nd layer line.	3rd layer line.	4th layer line.
Average length of c axis.	7.633	7.573	7.547	7.590

Length of the c axis is 7.586 A.U.

Length of the a axis is . . . . . .5.533 A.U.

Length of the b axis is . . . . . 17.66 A.U.

Length of the c axis is . . . . . 7.586 A.U.

---

a : b : c = 0.313 : 1 : 0.429

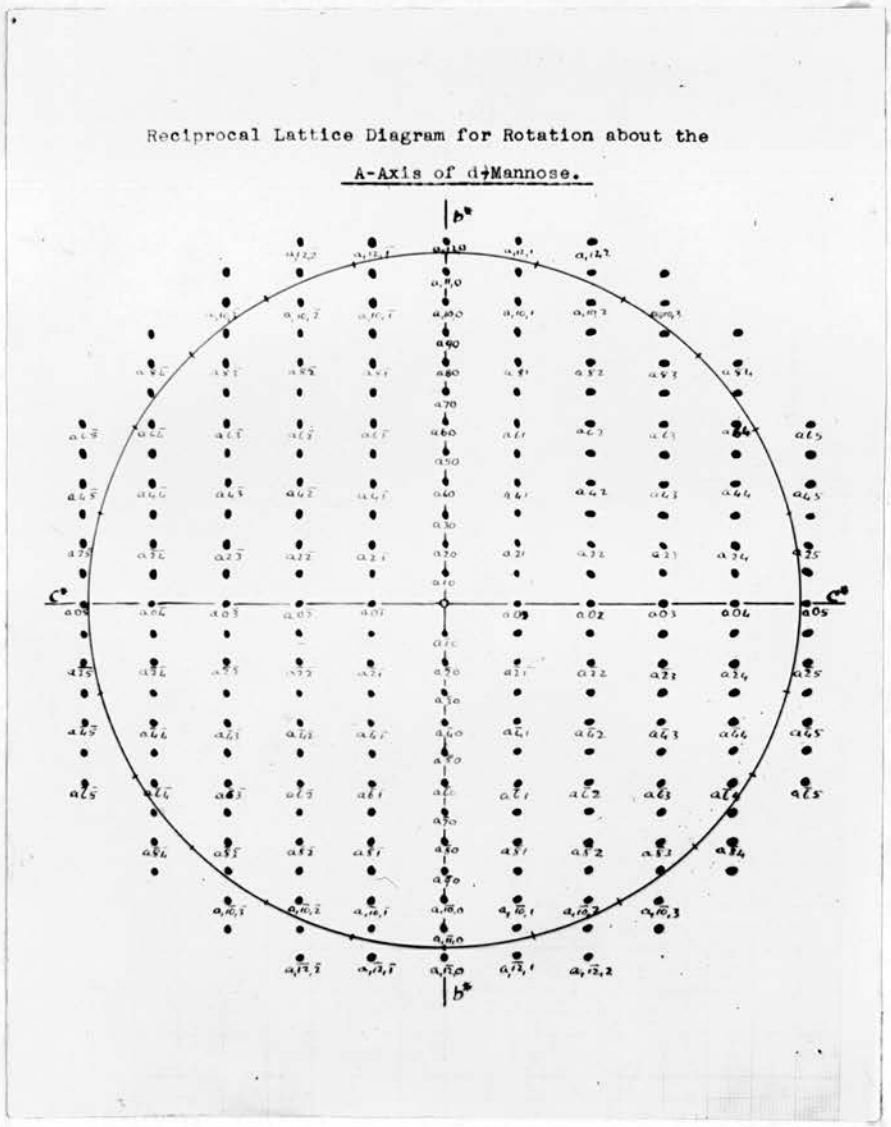

Reciprocal Lattice Diagram for Rotation about the
A-Axis of d-Mannose.
b*
c*
c*
b*

Figure 17.

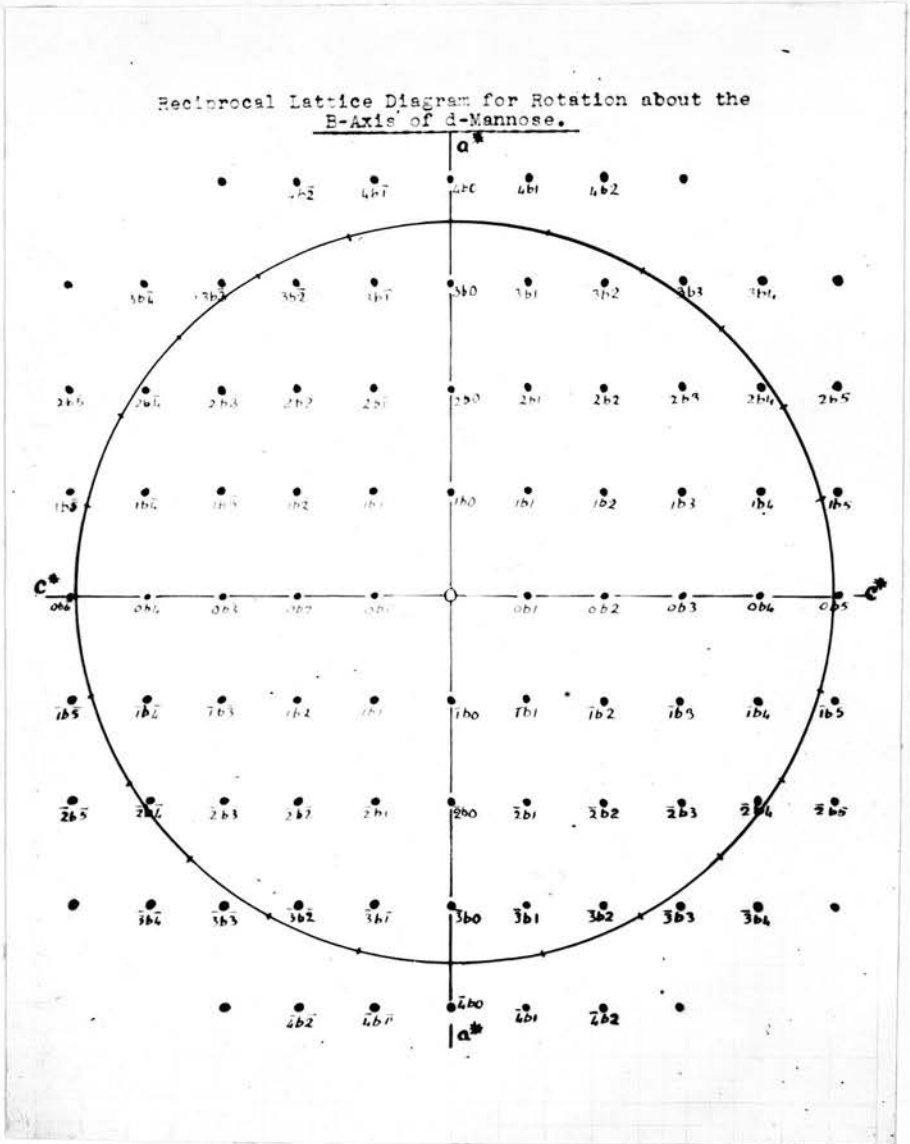

Reciprocal Lattice Diagram for Rotation about the
B-Axis of d-Mannose.
a*
c*
c*
a*

Figure 18.

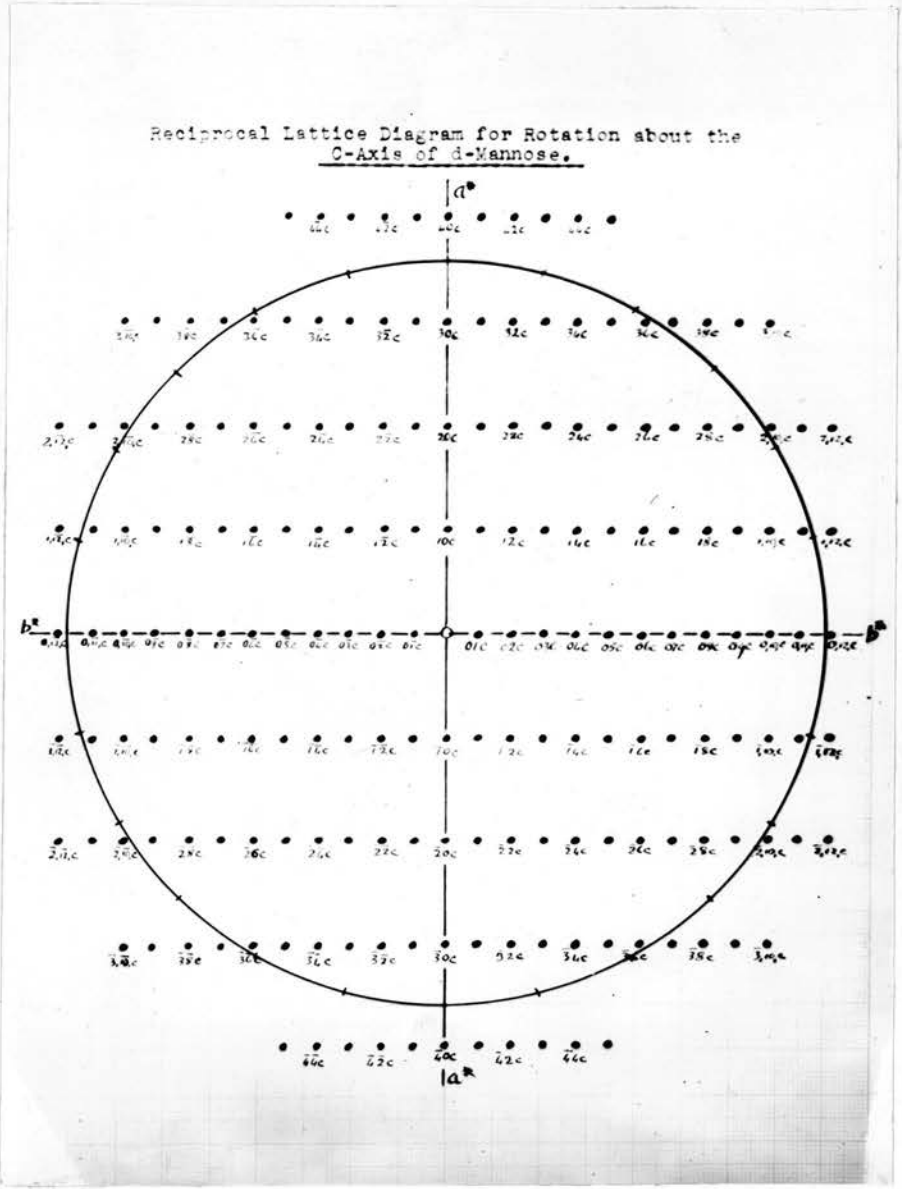

Reciprocal Lattice Diagram for Rotation about the C-Axis of d-Mannose.
a*
b*
b*
a*

Figure 19.

cell where

$$a^* = \lambda/a = 0.2775$$

$$b^* = \lambda/b = 0.08714$$

$$c^* = \lambda/c = 0.2029$$

A set of six oscillation photographs was made using each crystallographic axis in turn as the axis of oscillation. The reciprocal lattice diagrams were used to determine the planes which came into the reflecting position during each oscillation.

Calculation of the theoretical spacings of all reflecting planes was made by means of equation (VIII) (page 35). These values are given in the second column of Table IV (pages 56 to 58) under the heading of "Calculated Spacings". The values of the spacings of the planes from which reflections were recorded on the photographs were calculated by means of equation (XV) from the co-ordinates of the spot on the photographs corresponding to the reflected beam of X-rays. These results are given in the third column of Table IV, and are the "Observed Spacings".

Reflections from nearly two hundred crystal planes were recorded, and the planes identified.

A comparison of the "Calculated" and "Observed" spacings shows that

(a) the odd order spectra of the (100), (010), and (001) planes were not observed,

(b) no doubling or halving of the spacings of any other planes was found, and

(c) reflections from the (0,11,2), (074), (1,11,0)

T A B L E (IV).

Plane Indices	Calc. Spacing	Obs. Spacing	Plane Indices	Calc. Spacing	Obs. Spacing
100	5.533		061	2.744	2.733
200	2.767	2.788	062	2.326	2.328
300	1.845		063	1.918	1.923
			064	1.595	1.591
010	17.66				
020	8.830	8.894	071	2.394	2.404
030	5.887		072	2.101	2.104
040	4.415	4.461	073	1.787	1.791
050	3.532		074	1.516	
060	2.943	2.960			
070	2.523		081	2.121	2.123
080	2.202	2.214	082	1.909	1.912
090	1.962		083	1.664	1.662
0,10,0	1.766	1.769	084		
0,11,0	1.605		091	1.899	1.897
			092	1.743	1.753
001	7.586		093	1.550	1.545
002	3.793	3.781			
003	2.529		0,10,1	1.720	1.723
004	1.897	1.893	0,10,2	1.601	1.597
			0,10,3	1.448	1.448
011	6.970	6.960			
012	3.709	3.692	0,11,1	1.571	1.570
013	2.504	2.501	0,11,2	1.478	
014	1.885	1.883			
			101	4.471	4.461
021	5.754	5.770	102	3.128	3.134
022	3.486	3.490	103	2.301	2.308
023	2.431	2.426	104	1.794	1.789
024	1.854	1.850			
			201	2.599	2.591
031	4.651	4.690	202	2.236	2.226
032	3.189	3.200	203	1.863	1.870
033	2.324	2.332	204	1.564	1.561
034	1.805	1.808			
			301	1.797	1.795
041	3.818	3.809	302	1.658	1.664
042	2.877	2.865	303	1.490	1.497
043	2.195	2.171			
044	1.743	1.741	110	5.281	5.325
			111	4.334	4.248
051	3.202	3.193	112	3.152	3.090
052	2.585	2.590	113	2.281	2.286
053	2.056	2.060	114	1.785	1.783
054	1.671	1.665			

Plane Indices	Calc. Spacing	Obs. Spacing	Plane Indices	Calc. Spacing	Obs. Spacing
120	4.689	4.720	210	2.734	2.750
121	3.988	4.007	211	2.572	2.575
122	2.949	2.952	212	2.218	2.238
123	2.226	2.279	213	1.856	1.857
124	1.758	1.759	214	1.559	1.551
130	4.032	4.082	220	2.640	2.745
131	3.561	3.600	221	2.494	2.500
132	2.763	2.775	222	2.167	2.147
133	2.142	2.150	223	1.826	1.830
134	1.716	1.725	224	1.576	1.542
140	3.452	3.465	230	2.505	2.523
141	3.142	3.144	231	2.328	2.393
142	2.553	2.554	232	2.090	2.110
143	2.040	2.041	233	1.779	1.797
144	1.661	1.656	234	1.512	1.516
150	2.977	2.983	240	2.345	2.362
151	2.771	2.770	241	2.246	2.250
152	2.343	2.344	242	1.994	1.996
153	1.928	1.927	243	1.719	1.722
154	1.596	1.596	244	1.475	1.472
160	2.599	2.603	250	2.179	2.184
161	2.458	2.460	251	2.094	2.102
162	2.145	2.143	252	1.888	1.902
163	1.812	1.813	253	1.650	1.653
164	1.532	1.525	254	1.431	1.432
170	2.297	2.314	260	2.016	2.036
171	2.198	2.201	261	1.949	1.945
172	1.965	1.965	262	1.780	1.795
173	1.700	1.701	263	1.577	1.579
174	1.462	1.453	264	1.383	1.382
180	2.052	2.053	270	1.864	1.871
181	1.980	1.977	271	1.811	1.814
182	1.804	1.804	272	1.678	1.685
183	1.593	1.594	273	1.501	1.502
			274	1.329	1.327
190	1.850	1.856			
191	1.797	1.796	280	1.726	1.727
192	1.662	1.663	281	1.683	1.682
193	1.493	1.492	282	1.571	1.574
			283	1.426	1.424
1100	1.683	1.684			
1101	1.643	1.644	290	1.601	1.608
1102	1.538	1.540	291	1.530	1.565
1103	1.401	1.367	292	1.475	1.485
			293	1.353	1.343
1110	1.542				
1111	1.511	1.512	2100	1.488	1.487
1112	1.429	1.431	2101	1.461	1.463
1113	1.316	1.318	2102	1.385	1.393

Plane Indices	Calc. Spacing	Obs. Spacing	Plane Indices	Calc. Spacing	Obs. Spacing
2,11,0	- 1.388 -	- 1.395	340	- 1.702 -	- 1.701
2,11,1	- 1.366 -	- 1.367	341	- 1.661 -	- 1.655
			342	- 1.518 -	- 1.560
310	- 1.835 -	- 1.842	343	- 1.412 -	- 1.418
311	- 1.783 -	- 1.781			
312	- 1.652 -	- 1.654	350	- 1.635	
313	- 1.485 -	- 1.488	351	- 1.598 -	- 1.594
			352	- 1.502 -	- 1.506
320	- 1.806 -	- 1.808			
321	- 1.757 -	- 1.759	360	- 1.563 -	- 1.567
322	- 1.630 -	- 1.683	361	- 1.531 -	- 1.530
323	- 1.469 -	- 1.472	362	- 1.445 -	- 1.446
330	- 1.760 -	- 1.765	370	- 1.489 -	- 1.493
331	- 1.715 -	- 1.718	371	- 1.461 -	- 1.459
332	- 1.597 -	- 1.598	372	- 1.386 -	- 1.351
333	- 1.445 -	- 1.445			

and the (350) planes were too weak to affect the photographic film and the spots corresponding to the reflections were not observed.

It will be seen that the only abnormal spacings are those belonging exclusively to the axial zones. The Bravais lattice is therefore the simple lattice Γ_o.

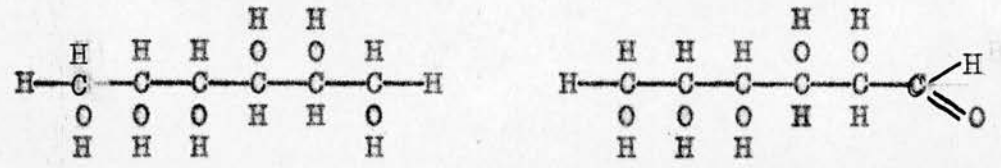
Reference to the tabulated data of Astbury and Yardley (loc. cit.) shows that in a crystal belonging to the rhombic bisphenoidal class, and having the (100) (010), and (001) planes halved the space-group is Q^4.

The molecules in the unit cell of a crystal belonging to this space-group must be asymmetric, and in this case the crystal molecule is identical with the chemical molecule. The chemical molecule must therefore be asymmetric. This fact, however, does not point to any particular structure for the molecule of d-mannose, since the molecule is asymmetric whether it have a straight chain or a ring structure.

In order to distinguish between a possible straight chain or a ring structure attention must be given to the relative intensities of the reflections from the crystal planes.

It has been shown that the molecule of d-mannitol possesses a straight chain structure. A comparison of the molecules of d-mannitol and d-mannose shows that replacement by an aldehyde grouping of the terminal primary hydroxyl group attached to carbon atom 6 (numbering from left to right in figure 20,A) in the molecule of d-mannitol yields one configuration for the

molecule of d-mannose.



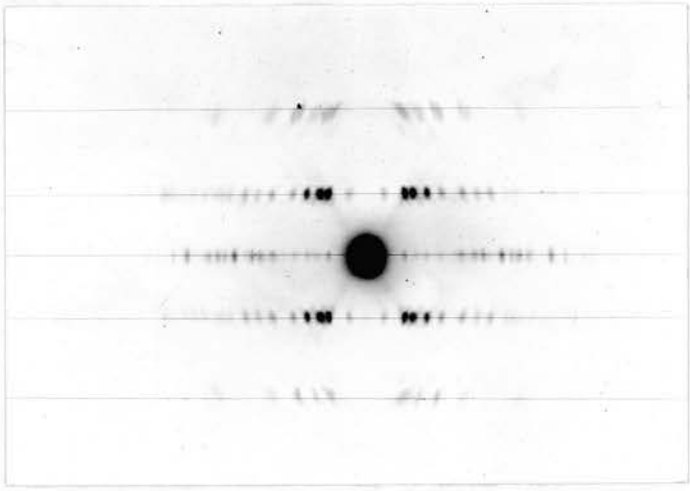
(A). (B).

Figure 20.

Such a slight change in the structure of the molecule might be expected to produce a correspondingly small change in the distribution of the intensity of the reflected beams of X-rays.

If, however, the molecule possesses a ring structure the atoms comprising the molecule will occupy different positions within the unit cell, and consequently a different intensity of the beam of X-rays reflected from certain planes will result. From the reproductions of the rotation photographs taken about the b and c axes of d-mannitol, and about the b and a axes of d-mannose given in figure 21, it will be seen that there is a peculiar distribution of the intensity of the reflected rays in the case of the b axis rotation photographs of d-mannose. This distribution of intensity is so different from that found in the corresponding photograph of d-mannitol that it cannot be reconciled with a straight chain molecule almost exactly similar to that of d-mannitol. The molecule of d-mannose most probably possesses a ring structure.

A comparison of the lengths of the corresponding sides of the unit cells of the crystals of d-mannitol and d-mannose is interesting. It has already been



Rotation photograph about the
a axis of d-mannose.

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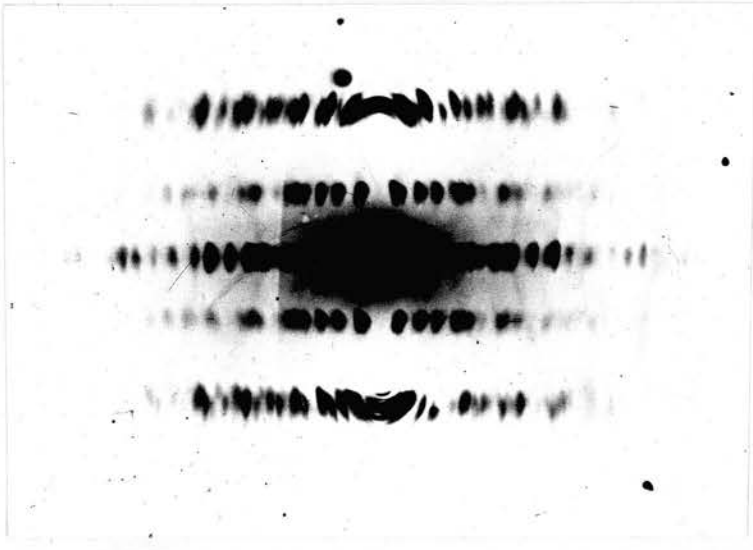
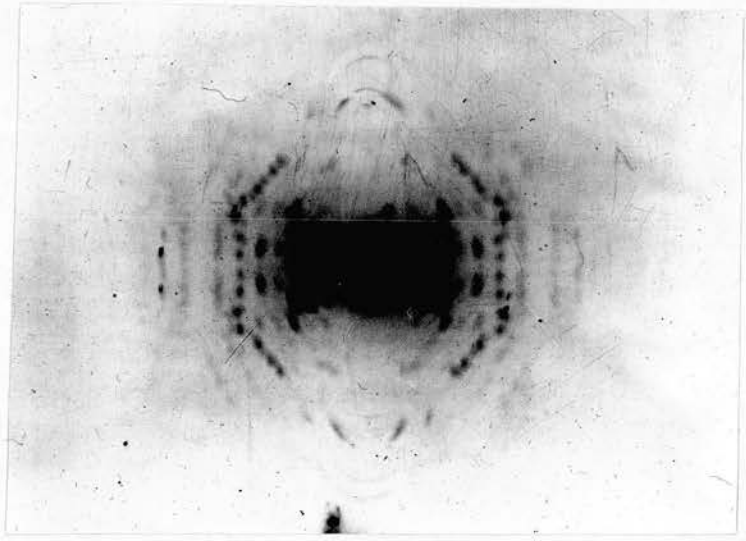
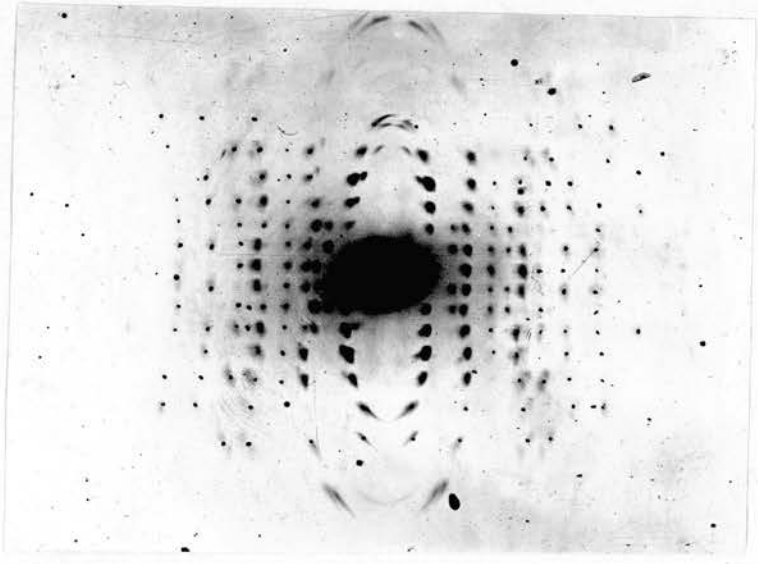


Rotation photograph about
the c axis of d-mannitol.

Figure 21.



Rotation photograph about the
b axis of d-mannose.



Rotation photograph about the
b axis of d-mannitol.

Figure 21.

mentioned that the c axis of d-mannose corresponds to the a axis of d-mannitol, and for convenience the respective values are given in Table V as the lengths of the a axis in both cases.

TABLE V.

	a axis	Difference.	b axis	Difference	c axis	Difference.
d-mannitol	8.664	−1.08	16.58	+1.08	5.501	+0.03
d-mannose	7.586		17.66		5.533	

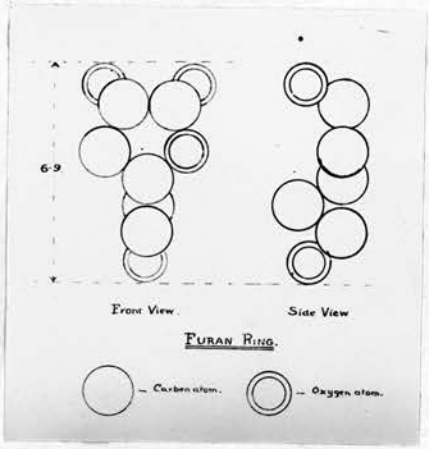
The construction of a model of the molecule of d-mannitol shows that the length of the molecule corresponds almost exactly with the length of the a axis when the molecule is considered to have a chain structure. The a axis of d-mannose is shorter than that of d-mannitol, while there is an increase in the length of the other two axes. This might mean that the molecule of d-mannose has a ring structure, since the formation of a ring would tend to reduce the length and to increase the width of the molecule without causing any considerable change in the thickness.

Thus the results of the X-ray examination show that a ring structure is more probable in d-mannose than a straight chain structure. It is still necessary to distinguish between a furan and a pyran ring structure.

The atoms composing the ring are considered to lie in one plane since such an arrangement would be more stable than a "puckered" ring structure where the atoms do not lie in one plane. In order that the tetrahedral nature of the carbon atom be preserved it is then

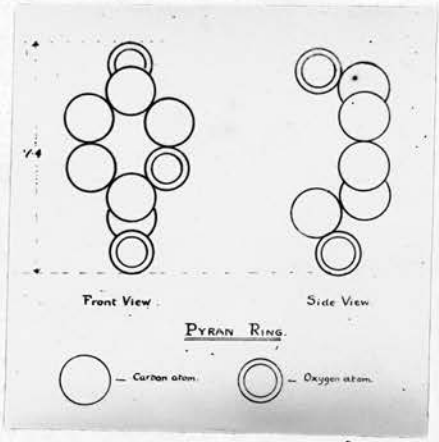
necessary that the carbon atoms in the side-chain should have a "zig-zag" arrangement similar to that of the atoms in the long chain hydrocarbons.

Figures 22a, 22b, 23a, and 23b show front and side views of a furan and a pyran ring structure respectively. The diagrams are drawn to scale, and on measurement of the length of the molecule in each case, it was found



a. b.

Figure 22.



a. b.

Figure 23.

that in the furan ring structure the molecule measured only 6.9 A.U., while in the pyran structure the molecule measured 7.4 A.U. The length of the side of the unit cell of the crystal corresponding to the length of the molecule was found to be 7.58 A.U. It seems, therefore, more probable that the molecule of d-mannose possesses a pyran ring structure than a furan ring structure.

While the foregoing argument is not a definite proof of the structure of d-mannose, it tends to corroborate previous examinations of the structure by chemical means.

SUMMARY.

The results of the X-ray analysis of d-mannose show that the lengths of the sides of the unit cell are a = 5.533 A.U., b = 17.66 A.U., c = 7.586 A.U. There are 4 molecules in the unit cell and the calculated density is 1.602 gms./c.c. The Bravais lattice is Γ_o, and the space-group is Q^4. The longest length of the crystal corresponded to the length c = 7.586 A.U. which may be compared with the a axis of d-mannitol. Reasons are given showing that a pyran ring structure is probable for the molecule of d-mannose.

NOTE.

In "Nature" of the 12th. January 1931 a letter was published in which Miss Thora C. Marwick gave a summary of results obtained in an X-ray analysis of d-mannitol and d-mannose.

d-MANNITOL: a = 8.65 A.U., b = 16.90 A.U., c = 5.56 A.U.; Bravais lattice, Γ_o; space-group, Q^4; 4 molecules in the unit cell; calculated density, 1.497 gms./c.c.

d-MANNOSE: a = 7.62 A.U., b = 18.18 A.U., c = 5.67 A.U.; Bravais lattice, Γ_o; space-group, Q^4; 4 molecules in the unit cell; calculated density, 1.501 gms./c.c.

The greatest length of the molecule was found to be parallel to the a axis in both cases, and a pyran ring structure was given as the probable structure of the molecule of d-mannose.

The results set out in this Thesis agree with those obtained by Miss Marwick although differing slightly in the actual lengths of the sides of the unit cells. The work was carried out simultaneously.

In conclusion, the author wishes to express his very grateful thanks to Sir James Walker, D.Sc., F.R.S. and to Professor James Kendall for their very helpful criticism and advice. The author's thanks are due also to The Department of Scientific and Industrial Research, and to The Carnegie Trust for the Universities of Scotland for their financial assistance, which enabled him to carry out the work.